Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Iridium(III)- and Rhodium(III)-Catalyzed Coupling of Anilines with α-Diazoesters *via* Chelation-Assisted C-H Activation

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Contents

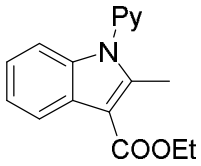
1. General Remarks

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using sealed tube. NMR Spectra were recorded on a Bruker 400 MHz or 500 MHz NMR spectrometer in the solvents indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained on an Agilent Q-TOF 6540 spectrometer. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE). *N*-phenylpyridin-2-amine derivatives,[1,2] *N*-phenylpyrimidin-2-amine,[3] and diazo esters[4] were prepared according to literature reports.

2. General Procedure and Characterization Data

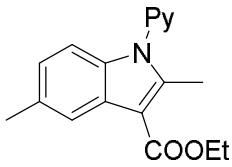
General procedure for the preparation of ethyl 2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (3aa)

A mixture of *N*-phenylpyridin-2-amine **1a** (51 mg, 3 mmol, 1.0 equiv), $[IrCp^*Cl_2]_2$ (6 mg, 0.0075mmol, 2.5 mol%) and CsOAc (14.4 mg, 0.075 mmol, 25 mol%) were weighted into a pressure tube equipped with a stir bar. Water (2 mL), EtOH (1 mL), HOAc (9 mg, 0.15 mmol, 50 mol%) and ethyl diazoacetoacetate **2a** (70.2 mg, 0.45 mmol, 1.5 equiv) were added successively. The mixture was stirred in a sealed tube at 100 ^{o}C for 5 h under air. Afterwards, it was cooled to room temperature, and water was removed under reduced pressure and the solid residue was purified by column chromatography to afford pure product **3aa** (74.8 mg, 89% yield).



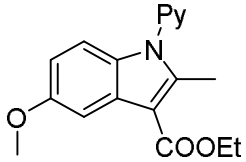
Ethyl 2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3aa**) 89% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.70 (d, *J* = 4.7 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.92 (t, *J* = 7.7 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.23 – 7.14 (m, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.71 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 166.1, 150.2, 150.0, 145.1, 138.7, 136.7, 126.8, 123.4, 122.8, 122.4, 122.2, 121.5, 110.4, 106.3, 59.7, 14.6, 13.2. HRMS $[M + H]^+$ calculated for $C_{17}H_{17}N_2O_2$: 281.1285, found 281.1287.



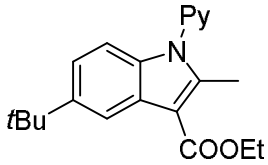
Ethyl 2,5-dimethyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3ba**) 78% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.70 (d, *J* = 3.8 Hz, 1H), 7.98 (s, 1H), 7.92 (td, *J* = 7.7, 1.6 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 2.48 (s, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 150.4, 150.0, 144.9, 138.6, 135.0, 131.8, 127.1, 124.2, 123.2, 122.0, 121.3, 110.0, 105.9, 59.6, 21.7, 14.7, 13.. HRMS $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_2$: 295.1441, found 295.1443.



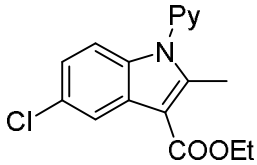
Ethyl 5-methoxy-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3ca**) 87% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.58 (d, *J* = 4.2 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.36 – 7.21 (m, 2H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.71 (dd, *J* = 8.9 Hz, 2.1 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.79 (s, 3H), 2.59 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 156.0, 150.2, 150.0, 145.1, 138.6, 131.6, 127.7, 123.3, 122.0, 112.3, 111.2, 106.0, 103.6, 59.6, 55.7, 14.6, 13.4. HRMS $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_3$: 311.1390, found 311.1391.



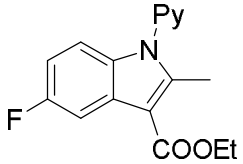
Ethyl 5-(tert-butyl)-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3da**) 65% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.7, 1.0 Hz, 1H), 8.25 (d, *J* = 1.3 Hz, 1H), 7.91 (td, *J* = 7.7, 1.9 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.26 (dd, *J* = 8.6 Hz, 1.6 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 150.4, 150.0, 145.4, 145.0, 138.5, 134.8, 126.7, 123.2, 121.9, 120.9, 117.6, 109.9, 106.3, 59.6, 34.8, 31.9, 14.6, 13.3. HRMS $[M + H]^+$ calculated for $C_{21}H_{25}N_2O_2$: 337.1911, found 337.1913.



Ethyl 5-chloro-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3ea**) 67% yield

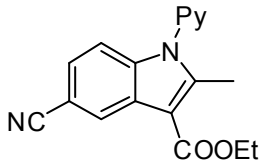
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 4.8, 1.1 Hz, 1H), 8.15 (s, 1H), 7.94 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 (dd, *J* = 7.2, 5.1 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 0.9 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 150.1, 149.8, 146.1, 138.8, 135.0, 128.1, 127.9, 123.7, 123.0, 122.0, 121.1, 111.5, 105.9, 59.9, 14.6, 13.3. HRMS $[M + H]^+$ calculated for $C_{17}H_{16}N_2O_2Cl$: 315.0895, found 315.0897.



Ethyl 5-fluoro-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3fa**) 87% yield

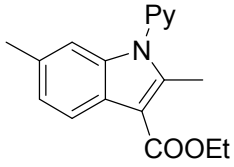
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.68 (m, 1H), 7.95 (td, *J* = 7.8, 1.8 Hz, 1H), 7.83 (dd, *J* = 9.9, 2.5 Hz, 1H), 7.44 (dd, *J* = 7.4, 5.0 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.13 (dd, *J* = 8.9, 4.4 Hz, 1H), 6.90 (td, *J* = 9.0, 2.5 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 159.4 (d, *J* = 235 Hz), 150.1, 150.0, 146.4, 138.8, 133.1, 127.6 (d, *J* = 11.0 Hz), 123.6, 122.0, 111.2 (d, *J* = 9.6 Hz), 110.8 (d, *J* = 25.9 Hz) 107.0 (d, *J* = 25.3 Hz), 106.3 (d, *J* = 4.0 Hz),

59.8, 14.6, 13.3. HRMS $[M + H]^+$ calculated for $C_{17}H_{16}N_2O_2F$: 299.1190, found 299.1190.



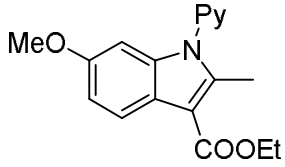
Ethyl 5-cyano-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3ga**) 67% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.6 Hz, 1H), 8.52 (s, 1H), 8.01 (t, *J* = 7.7 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.22 (m, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.71 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 150.4, 149.2, 147.3, 139.1, 138.2, 126.9, 126.6, 125.9, 124.15, 122.1, 120.4, 111.4, 106.6, 105.6, 60.2, 14.6, 13.2. HRMS $[M + H]^+$ calculated for $C_{18}H_{16}N_3O_2$: 306.1237, found 306.1238.



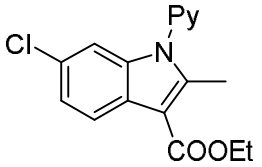
Ethyl 2,6-dimethyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3ha**) 85% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.2 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.91 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.99 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 2.39 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 150.3, 150.0, 144.6, 138.6, 137.0, 132.7, 124.6, 124.0, 123.3, 122.2, 121.2, 110.4, 106.1, 77.4, 77.1, 76.8, 59.6, 21.7, 14.6, 13.2. HRMS $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_2$: 295.1441, found 295.1444.



Ethyl 6-methoxy-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3ia**) 63% yield

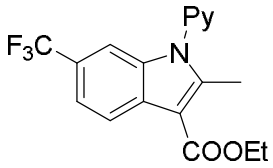
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 3.7 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.98 – 7.92 (m, 1H), 7.46 – 7.37 (m, 2H), 6.91 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.71 (d, *J* = 2.1 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 2.67 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 156.8, 150.3, 150.1, 144.0, 138.7, 137.4, 123.4, 122.1, 122.1, 120.9, 111.2, 106.2, 94.7, 59.6, 55.7, 14.6, 13.2. HRMS $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_3$: 311.1390, found 311.1392.



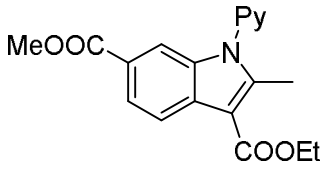
Ethyl 6-chloro-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**2ja**) 82% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.95 (td, *J* = 7.7, 1.9 Hz, 1H), 7.44 (ddd, *J* = 7.5, 4.9, 0.8 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 150.1, 149.6, 145.5, 138.8, 136.9, 128.6, 125.3, 123.6, 122.9, 122.4, 122.0, 110.5, 106.3, 59.8, 14.5, 13.2.

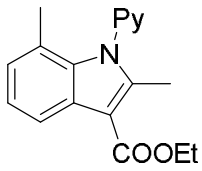
HRMS $[M + H]^+$ calculated for $C_{17}H_{16}N_2O_2Cl$: 315.0895, found 315.0893.



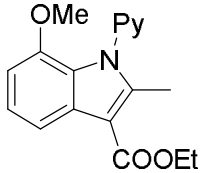
Eethyl 2-methyl-1-(pyridin-2-yl)-6-(trifluoromethyl)-1H-indole-3-carboxylate (**3ka**) 83% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 3.7 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.98 (td, *J* = 7.8, 1.7 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.40 (d, *J* = 7.9 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.72 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 150.3, 149.4, 147.4, 138.9, 135.7, 129.3, 124.9 (*J* = 270.0), 124.8 (*J* = 31.9 Hz), 123.9, 122.1, 121.9, 119.0 (*J* = 3.5 Hz), 107.9 (*J* = 4.3 Hz), 106.4, 59.9, 14.5, 13.2. HRMS $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_2$: 349.1158, found 349.1159.



3-ethyl 6-methyl 2-methyl-1-(pyridin-2-yl)-1H-indole-3,6-dicarboxylate (**3la**) 90% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 3.8 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.02 – 7.93 (m, 2H), 7.90 (s, 1H), 7.48 (dd, *J* = 7.4, 5.0 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 2.72 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 165.6, 150.3, 149.6, 148.0, 139.0, 136.1, 130.6, 124.5, 123.9, 123.5, 122.3, 121.1, 112.5, 106.6, 59.9, 52.0, 14.6, 13.4. HRMS $[M + H]^+$ calculated for $C_{19}H_{19}N_2O_4$: 339.1339, found 339.1337.

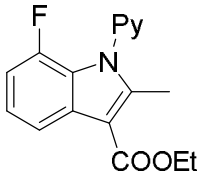


Ethyl 2,7-dimethyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3ma**) 93% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.1 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.1 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 2H), 2.49 (s, 3H), 1.76 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 152.1, 149.5, 145.6, 138.2, 135.6, 127.3, 125.5, 124.4, 124.3, 122.1, 121.0, 119.5, 105.5, 59.6, 19.0, 14.6, 12.7. HRMS $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_2$: 295.1441, found 295.1440.

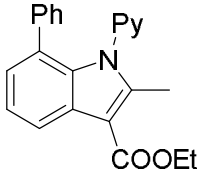


Ethyl 7-methoxy-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3na**) 85% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 3.4 Hz, 1H), 7.82 (t, *J* = 8.4 Hz, 2H), 7.46 – 7.35 (m, 1H), 7.34 – 7.24 (m, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.41 (q, *J* = 6.9 Hz, 2H), 3.52 (s, 3H), 2.52 (s, 3H), 1.45 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 152.1, 148.5, 146.4, 145.6, 137.4, 128.7, 126.2, 123.6, 123.4, 122.4, 114.2, 105.9, 104.4, 59.5, 55.5, 14.6, 12.6. HRMS [M

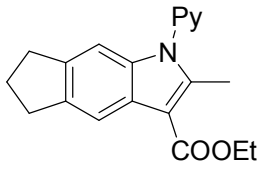
+ H]$^+$ calculated for $C_{18}H_{19}N_2O_3$: 311.1390, found 311.1391.



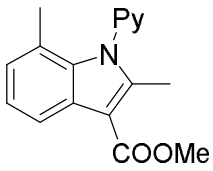
Ethyl 7-fluoro-2-methyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3oa**) 70% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.8, 0.9 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.97 (td, *J* = 7.8, 1.8 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.21 (td, *J* = 8.0, 4.6 Hz, 1H), 6.93 (dd, *J* = 12.1, 8.0 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.74, 150.81, 150.34, 150.34, 149.29, 147.90, 147.90, 146.43, 138.27, 130.34, 130.30, 124.3(*J* = 9.1 Hz), 123.97, 122.9 (*J* = 3.5 Hz), 122.3 (*J* = 3.5 Hz), 117.3 (*J* = 3.6 Hz), 108.75, 108.57, 106.64, 59.83, 14.57, 12.74. HRMS [M + H]$^+$ calculated for $C_{17}H_{16}N_2O_2F$: 299.1190, found 299.1192.



Ethyl 2-methyl-7-phenyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3pa**) 66% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 3.4 Hz, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.98 (dt, *J* = 119.1, 60.4 Hz, 7H), 6.67 (t, *J* = 10.9 Hz, 1H), 4.46 (q, *J* = 6.9 Hz, 2H), 2.58 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.12, 150.53, 148.52, 146.60, 139.24, 137.01, 133.70, 127.94, 127.47, 126.73, 125.98, 125.57, 123.65, 122.84, 122.00, 120.79, 105.99, 77.40, 77.08, 76.77, 59.71, 14.65, 13.06. HRMS [M + H]$^+$ calculated for$C_{23}H_{21}N_2O_2$: 357.1598, found 357.1601.

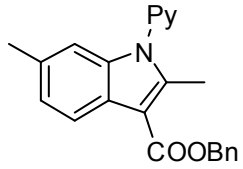


Ethyl 2-methyl-1-(pyridin-2-yl)-1,5,6,7-tetrahydrocyclopenta[f]indole-3-carboxylate (**3qa**) 76% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.06 (s, 1H), 8.00 (td, *J* = 7.7, 1.9 Hz, 1H), 7.48 (M, *J* = 13.8, 8.9, 4.4 Hz, 2H), 7.11 (s, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 3.08 (t, *J* = 7.3 Hz, 2H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.75 (s, 3H), 2.17 (p, *J* = 7.3 Hz, 2H), 1.54 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 150.5, 149.9, 144.2, 139.6, 139.0, 138.5, 136.2, 125.8, 123.1, 122.2, 116.4, 105.8, 59.5, 32.9, 32.6, 26.4, 14.6, 13.2. HRMS [M + H]$^+$ calculated for $C_{20}H_{21}N_2O_2$: 321.1598, found 321.1599.



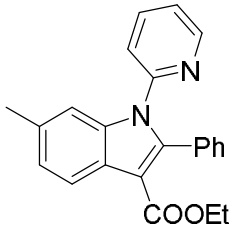
Methyl 2,7-dimethyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3mb**) 89% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 3.9 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.83 (m, 1H), 7.47 (dd, *J* = 7.2, 5.1 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 3.95 (s, 3H), 2.49 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 152.1, 149.5, 145.6, 138.2, 135.6, 127.1, 125.4, 124.4, 124.3, 122.1, 120.9, 119.4, 105.4, 50.8, 18.88, 12.7. HRMS $[M + H]^+$ calculated for$C_{17}H_{17}N_2O_2$: 281.1285, found 281.1284.



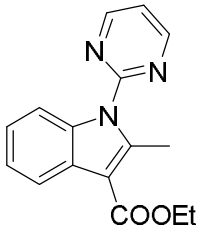
Benzyl 2,6-dimethyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3hc**) 92% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.7, 1.2 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.93 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.43 – 7.30 (m, 5H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.99 (s, 1H), 5.44 (s, 2H), 2.68 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 150.2, 150.1, 144.9, 138.6, 137.0, 137.0, 132.8, 128.6, 128.0, 127.9, 124.5, 124.1, 123.4, 122.2, 121.2, 110.4, 105.8, 65.5, 21.7, 13.3. HRMS $[M + H]^+$ calculated for$C_{17}H_{17}N_2O_2$: 357.1598, found 357.1600.



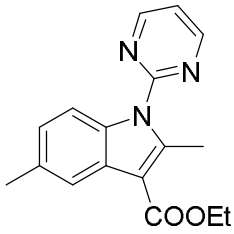
Ethyl 6-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3hd**) 82% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 4.8, 1.1 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.56 (td, *J* = 7.8, 1.8 Hz, 1H), 7.36 – 7.14 (m, 8H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.8, 149.3, 144.7, 137.9, 137.4, 133.8, 131.4, 131.1, 128.5, 127.6, 124.8, 124.6, 122.7, 122.6, 121.7, 111.3, 107.3, 59.7, 21.8, 14.3. HRMS $[M + H]^+$ calculated for$C_{17}H_{17}N_2O_2$: 357.1598, found 357.1600.



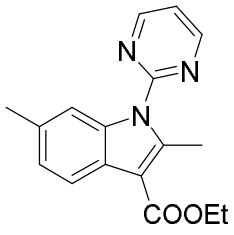
Ethyl 2-methyl-1-(pyrimidin-2-yl)-1H-indole-3-carboxylate (**3ra**) 87% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.1 Hz, 2H), 8.18 (d, *J* = 7.3 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.27 (m, 3H), 4.45 (q, *J* = 13.6, 6.6 Hz, 2H), 2.95 (s, 3H), 1.48 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 158.6, 157.3, 145.6, 136.0, 127.2, 123.3, 123.0, 121.4, 118.8, 112.5, 108.3, 59.9, 14.59, 14.3. HRMS $[M + H]^+$ HRMS $[M + H]^+$ calculated for $C_{17}H_{18}N_3O_2$: 282.1237, found 282.1235.



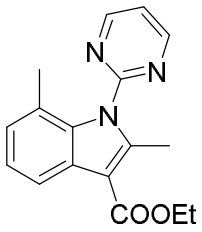
Ethyl 2,5-dimethyl-1-(pyrimidin-2-yl)-1H-indole-3-carboxylate (**3sa**) 80% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.8 Hz, 2H), 7.97 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 4.8 Hz, 2H), 7.13 – 7.03 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.94 (s, 3H), 2.48 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 158.5, 157.4, 145.5, 134.3, 132.4, 127.4, 124.7, 121.2, 118.6, 112.2, 108.1, 59.8, 21.7, 14.6, 14.5. HRMS $[M + H]^+$ calculated for $C_{17}H_{18}N_3O_2$: 296.1394, found 296.1396.



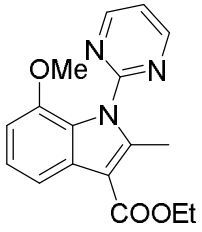
Ethyl 2,6-dimethyl-1-(pyrimidin-2-yl)-1H-indole-3-carboxylate (**3ta**) 83% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 4.4 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.36 (s, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 4.51 (q, *J* = 6.7 Hz, 2H), 2.99 (s, 3H), 2.53 (s, 3H), 1.54 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.06, 158.5, 157.3, 144.9, 136.3, 133.1, 124.9, 124.5, 121.0, 118.7, 112.3, 108.2, 104.9, 59.7, 21.8, 14.5, 14.2. HRMS $[M + H]^+$ calculated for $C_{17}H_{18}N_3O_2$: 296.1394, found 296.1393.

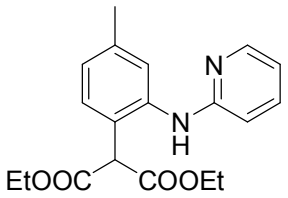


Ethyl 2,7-dimethyl-1-(pyrimidin-2-yl)-1H-indole-3-carboxylate (**3ua**) 67% yield

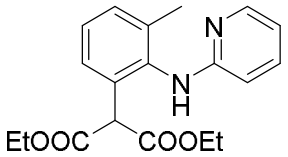
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.6 Hz, 2H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 4.5 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 6.9 Hz, 1H), 4.42 (q, *J* = 6.9 Hz, 2H), 2.58 (s, 3H), 1.80 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 158.8, 158.5, 145.5, 135.5, 127.3, 125.7, 122.4, 120.9, 120.6, 119.6, 106.3, 59.7, 19.1, 14.6, 12.7. HRMS $[M + H]^+$ calculated for $C_{17}H_{18}N_3O_2$: 296.1394, found 296.1395.



Ethyl 7-methoxy-2-methyl-1-(pyrimidin-2-yl)-1H-indole-3-carboxylate (**3va**) 73% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.3 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.36 (s, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 4.42 (q, *J* = 6.7 Hz, 2H), 3.55 (s, 3H), 2.68 (d, *J* = 64.2 Hz, 3H), 1.45 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 158.3, 146.2, 145.2, 128.7, 126.2, 122.8, 120.2, 114.3, 106.4, 104.7, 59.7, 55.8, 29.7, 14.6, 12.5. HRMS $[M + H]^+$ calculated for $C_{17}H_{18}N_3O_3$: 312.1343, found 312.1342.



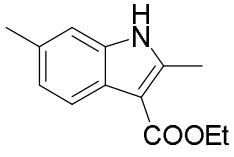
Diethyl 2-(4-methyl-2-(pyridin-2-ylamino)phenyl)malonate (**5ha**) 67% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.3 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.11 (s, 1H), 6.69 – 6.56 (m, 1H), 6.09 (d, *J* = 8.3 Hz, 1H), 4.03 (m, 4H) 2.20 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 157.0, 148.2, 137.7, 137.5, 136.8, 132.5, 131.4, 128.5, 126.8, 113.9, 106.9, 61.8, 55.2, 18.8, 13.9. HRMS $[M + H]^+$ calculated for $C_{18}H_{21}N_2O_4$: 343.1652, found 343.1650.



Diethyl 2-(3-methyl-2-(pyridin-2-ylamino)phenyl)malonate (**5ma**) 54% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 3.8 Hz, 1H), 7.40 – 7.18 (m, 4H), 7.07 (s, 1H), 6.71 – 6.54 (m, 1H), 6.09 (d, *J* = 8.1 Hz, 1H), 4.87 (s, 1H), 4.10 – 3.88 (m, 4H), 2.20 (s, 3H), 1.17 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 157.0, 148.2, 137.7, 137.5, 136.8, 132.5, 131.4, 128.5, 126.8, 113.9, 106.9, 61.8, 55.2, 18.8, 13.9. HRMS $[M + H]^+$ calculated for $C_{18}H_{21}N_2O_4$: 343.1652, found 343.1653.

Representative Synthetic Procedure of 6.

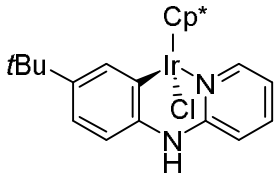
Ethyl 2,6-dimethyl-1-(pyridin-2-yl)-1H-indole-3-carboxylate (**3ha**, 88.2 mg, 0.3 mmol) was placed into a 20 mL two-necked reaction flask filled with nitrogen. The flask was cooled to 0 ˚C with an ice-water bath. CH_2Cl_2 (3 mL) and methy trifluoromethanesulfonate (36 μL, 0.32 mmol) were then added to the flask. The mixture was allowed to warm to room temperature and stirred for 20 h. All volatiles were evaporated under vacuum, and sodium *tert*-butoxide (87 mg, 0.9 mmol) was added, which was again filled with nitrogen by using the standard Schlenk technique. EtOH (0.6 mL) and Et_2O (2.4 mL) were added, and the resulting suspension was stirred for 4 h at room temperature. The mixture was quenched with water and extracted with Et_2O. The combined organic layer was dried over sodium sulfate. After concentration, column chromatographic purification afforded ethyl 2,6-dimethyl-1H-indole-3-carboxylate (**6**, 41 mg, 0.090 mmol) in 63% yield.



Ethyl 2,6-dimethyl-1H-indole-3-carboxylate (**6**)

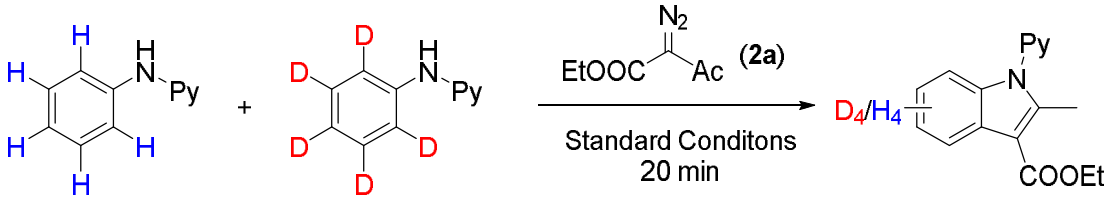
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.11 – 6.94 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.71 (s, 3H), 2.44 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 143.3, 134.9, 132.2, 125.0, 123.3, 121.0, 110.5, 104.5, 59.5, 21.6, 14.6, 14.2. HRMS $[M + H]^+$ calculated for $C_{13}H_{16}NO_2$: 218.1176, found 218.1174.

Synthetic Procedure of Complex 7. A mixtue of *N*-(4-(tert-butyl)-phenyl)pyridin-2-amine (0.2 mmol, 1 equiv), $[IrCp^*Cl_2]_2$ (0.5 eq), and NaOAc (1.1equiv) in 4 mL DCM was stirred under N_2 at RT overnight. After filtration, the solvent was removed. The residue was washed with Et_2O (10 mL *2) , then the solvent was remove to afford **7** in analytically pure form.



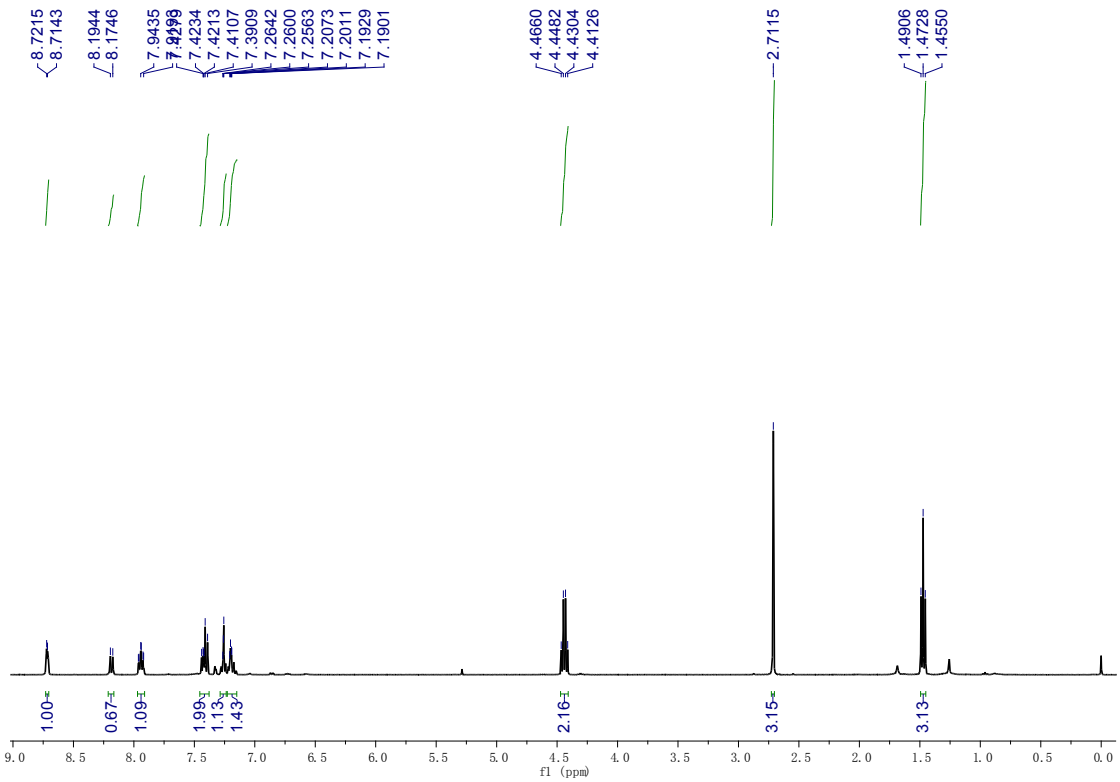
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.51 (d, *J* = 6.0 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.42 – 7.35 (m, 1H), 6.76 (dd, *J* = 8.0 Hz, 2.2, 1H), 6.60 – 6.47 (m, 3H), 6.31 (s, 1H), 1.46 (s, 15H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 154.8, 154.1, 145.9, 138.0, 137.1, 136.4, 131.3, 119.8, 116.0, 112.0, 111.3, 87.5, 31.67, 8.7. HRMS $[M - Cl]^+$ calculated for $C_{25}H_{32}N_2Ir$: 553.2195, found 553.2199.

3. KIE STUDIES



1a **1a**-d_5 KIE = 2.0

A mixture of *N*-phenylpyridin-2-amine (**1a**, 51.3 mg, 0.3 mmol, 1 equiv), *N*-(2, 3, 4, 5, 6-pentadeueriophenyl) pyridin-2-amine (**1a**-d_5, 52.5 mg, 0.6 mmol, 1 equiv), $[IrCp^*Cl_2]_2$ (6 mg, 0. 0075 mmol, 2.5 mol%) and CsOAc (14 mg, 0.075 mmol, 25 mol%) were weighted into a pressure tube equipped with a stir bar. Water (2 mL), EtOH (1 mL), HOAc (9 mg, 0.15 mmol, 50 mol%) and ethyl diazoacetoacetate (70 mg, 0.45 mmol, 1.5 equiv) were added successively. The mixture was stirred at 100 °C for 20 min. Afterwards, it was cooled in an ice bath and the mixture was filtered off immediately. The solid residue was washed with water thoroughly, and purified by passing through a short pad of silica gel with PE /EA as eluent. The ratio of **3aa**/ **3aa**-d_4 was indicated to be 2.0:1 by ^{1}H NMR analysis (see below), and the KIE value was determined to be 2.0.



4. Crystal data and Structure Refinement for Complex 7

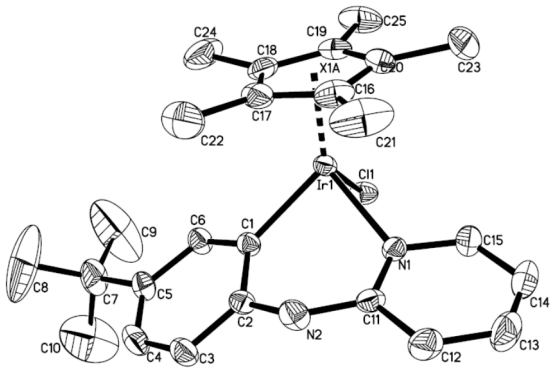


Table 1. Crystal data and structure refinement for complex 7.

Empirical formula	$C_{25}H_{32}ClIrN_2$
Formula weight	588.18
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 13.083(3) A alpha = 90 °.
	b = 9.848(2) A beta = 93.26(3) °.
	c = 18.876(4) A gamma = 90 °.
Volume	2428.2(8) A^3
Z, Calculated density	4, 1.609 Mg/m^3

Absorption coefficient	5.621 mm^{-1}
F(000)	1160
Crystal size	0.30 x 0.20 x 0.10 mm
Theta range for data collection	3.32 to 27.59 °.
Limiting indices	-17<=h<=17, -12<=k<=12, -24<=l<=24
Reflections collected / unique	48591 / 5599 [R(int) = 0.0422]
Completeness to theta	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5599 / 0 / 262
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR^2 = 0.0533
R indices (all data)	R1 = 0.0331, wR^2 = 0.0575
Largest diff. peak and hole	0.896 and -0.583 $e.A^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ir(1)	8177(1)	7670(1)	3975(1)	31(1)
Cl(1)	8034(1)	10091(1)	4135(1)	44(1)
N(1)	8811(2)	8005(3)	2990(1)	36(1)
N(2)	7564(2)	6703(3)	2373(1)	47(1)
C(1)	6790(3)	7681(3)	3413(2)	35(1)
C(2)	6703(2)	7136(3)	2733(2)	36(1)
C(3)	5752(3)	6976(4)	2379(2)	48(1)
C(4)	4881(3)	7340(4)	2706(2)	54(1)
C(5)	4919(3)	7915(4)	3373(2)	48(1)
C(6)	5891(3)	8094(4)	3706(2)	42(1)
C(7)	3941(3)	8294(5)	3726(3)	72(1)
C(8)	3310(7)	7036(11)	3791(7)	226(7)
C(9)	4098(5)	9065(11)	4383(4)	216(6)
C(10)	3291(5)	9228(10)	3245(4)	175(4)
C(11)	8496(3)	7284(3)	2414(2)	39(1)
C(12)	9136(3)	7121(4)	1842(2)	57(1)
C(13)	10062(4)	7769(5)	1867(3)	69(1)
C(14)	10353(3)	8576(4)	2440(2)	63(1)
C(15)	9722(3)	8658(4)	2986(2)	49(1)
C(16)	9019(3)	5818(4)	4178(2)	56(1)
C(17)	7987(3)	5681(4)	4386(2)	58(1)
C(18)	7855(3)	6655(4)	4942(2)	51(1)
C(19)	8811(3)	7314(3)	5072(2)	47(1)
C(20)	9528(3)	6806(4)	4624(2)	50(1)

C(21)	9517(5)	4996(5)	3628(2)	110(2)
C(22)	7196(5)	4671(5)	4110(3)	121(3)
C(23)	10643(4)	7190(6)	4616(3)	92(2)
C(24)	6941(4)	6803(7)	5382(3)	104(2)
C(25)	9024(4)	8404(5)	5626(2)	81(2)

Table S3. Bond lengths [A] and angles [deg] for complex **7**.

Ir(1)-C(1)	2.049(3)
Ir(1)-N(1)	2.106(3)
Ir(1)-C(17)	2.126(3)
Ir(1)-C(18)	2.143(3)
Ir(1)-C(16)	2.153(3)
Ir(1)-C(19)	2.214(4)
Ir(1)-C(20)	2.259(3)
Ir(1)-Cl(1)	2.4114(10)
N(1)-C(11)	1.343(4)
N(1)-C(15)	1.355(4)
N(2)-C(11)	1.346(5)
N(2)-C(2)	1.413(4)
N(2)-H(2A)	0.8600
C(1)-C(6)	1.388(5)
C(1)-C(2)	1.391(5)
C(2)-C(3)	1.388(5)
C(3)-C(4)	1.373(5)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.379(6)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.399(5)
C(5)-C(7)	1.523(6)
C(6)-H(6A)	0.9300
C(7)-C(9)	1.458(8)
C(7)-C(8)	1.497(10)
C(7)-C(10)	1.519(9)
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600

C(10)-H(10C)	0.9600
C(11)-C(12)	1.412(5)
C(12)-C(13)	1.369(7)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.378(6)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.360(5)
C(14)-H(14A)	0.9300
C(15)-H(15A)	0.9300
C(16)-C(20)	1.427(5)
C(16)-C(17)	1.434(6)
C(16)-C(21)	1.496(5)
C(17)-C(18)	1.439(6)
C(17)-C(22)	1.507(5)
C(18)-C(19)	1.419(6)
C(18)-C(24)	1.501(6)
C(19)-C(20)	1.392(6)
C(19)-C(25)	1.513(5)
C(20)-C(23)	1.507(6)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600

C(1)-Ir(1)-N(1)	85.59(12)
C(1)-Ir(1)-C(17)	94.31(13)
N(1)-Ir(1)-C(17)	121.77(15)
C(1)-Ir(1)-C(18)	103.42(14)
N(1)-Ir(1)-C(18)	158.71(13)
C(17)-Ir(1)-C(18)	39.40(15)
C(1)-Ir(1)-C(16)	121.70(14)
N(1)-Ir(1)-C(16)	93.82(13)
C(17)-Ir(1)-C(16)	39.14(16)

C(18)-Ir(1)-C(16)	64.98(15)
C(1)-Ir(1)-C(19)	139.35(15)
N(1)-Ir(1)-C(19)	134.89(14)
C(17)-Ir(1)-C(19)	63.81(13)
C(18)-Ir(1)-C(19)	37.96(15)
C(16)-Ir(1)-C(19)	62.56(14)
C(1)-Ir(1)-C(20)	157.72(13)
N(1)-Ir(1)-C(20)	101.69(12)
C(17)-Ir(1)-C(20)	63.87(14)
C(18)-Ir(1)-C(20)	63.17(14)
C(16)-Ir(1)-C(20)	37.63(15)
C(19)-Ir(1)-C(20)	36.24(14)
C(1)-Ir(1)-Cl(1)	89.23(9)
N(1)-Ir(1)-Cl(1)	89.60(8)
C(17)-Ir(1)-Cl(1)	148.60(13)
C(18)-Ir(1)-Cl(1)	109.53(11)
C(16)-Ir(1)-Cl(1)	149.04(12)
C(19)-Ir(1)-Cl(1)	93.86(9)
C(20)-Ir(1)-Cl(1)	111.64(11)
C(11)-N(1)-C(15)	118.5(3)
C(11)-N(1)-Ir(1)	121.0(2)
C(15)-N(1)-Ir(1)	118.0(2)
C(11)-N(2)-C(2)	126.0(3)
C(11)-N(2)-H(2A)	117.0
C(2)-N(2)-H(2A)	117.0
C(6)-C(1)-C(2)	117.0(3)
C(6)-C(1)-Ir(1)	122.7(2)
C(2)-C(1)-Ir(1)	120.0(2)
C(3)-C(2)-C(1)	120.8(3)
C(3)-C(2)-N(2)	116.9(3)
C(1)-C(2)-N(2)	122.3(3)
C(4)-C(3)-C(2)	119.9(3)
C(4)-C(3)-H(3A)	120.0
C(2)-C(3)-H(3A)	120.0
C(3)-C(4)-C(5)	122.0(3)
C(3)-C(4)-H(4A)	119.0
C(5)-C(4)-H(4A)	119.0
C(4)-C(5)-C(6)	116.5(3)
C(4)-C(5)-C(7)	120.9(4)
C(6)-C(5)-C(7)	122.5(4)
C(1)-C(6)-C(5)	123.7(3)
C(1)-C(6)-H(6A)	118.2
C(5)-C(6)-H(6A)	118.2
C(9)-C(7)-C(8)	114.4(7)

C(9)-C(7)-C(10)	103.9(6)
C(8)-C(7)-C(10)	104.9(7)
C(9)-C(7)-C(5)	114.7(4)
C(8)-C(7)-C(5)	108.3(5)
C(10)-C(7)-C(5)	110.0(5)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(1)-C(11)-N(2)	120.5(3)
N(1)-C(11)-C(12)	120.7(3)
N(2)-C(11)-C(12)	118.8(3)
C(13)-C(12)-C(11)	118.9(4)
C(13)-C(12)-H(12A)	120.5
C(11)-C(12)-H(12A)	120.5
C(12)-C(13)-C(14)	120.0(4)
C(12)-C(13)-H(13A)	120.0
C(14)-C(13)-H(13A)	120.0
C(15)-C(14)-C(13)	118.5(4)
C(15)-C(14)-H(14A)	120.8
C(13)-C(14)-H(14A)	120.8
N(1)-C(15)-C(14)	123.2(4)
N(1)-C(15)-H(15A)	118.4
C(14)-C(15)-H(15A)	118.4
C(20)-C(16)-C(17)	108.6(3)
C(20)-C(16)-C(21)	124.8(5)
C(17)-C(16)-C(21)	126.4(4)
C(20)-C(16)-Ir(1)	75.2(2)
C(17)-C(16)-Ir(1)	69.4(2)
C(21)-C(16)-Ir(1)	125.0(3)

C(16)-C(17)-C(18)	106.9(3)
C(16)-C(17)-C(22)	127.3(5)
C(18)-C(17)-C(22)	125.7(5)
C(16)-C(17)-Ir(1)	71.5(2)
C(18)-C(17)-Ir(1)	70.9(2)
C(22)-C(17)-Ir(1)	125.0(3)
C(19)-C(18)-C(17)	106.9(3)
C(19)-C(18)-C(24)	125.6(4)
C(17)-C(18)-C(24)	126.9(5)
C(19)-C(18)-Ir(1)	73.7(2)
C(17)-C(18)-Ir(1)	69.66(19)
C(24)-C(18)-Ir(1)	128.9(3)
C(20)-C(19)-C(18)	110.4(3)
C(20)-C(19)-C(25)	124.8(4)
C(18)-C(19)-C(25)	124.8(4)
C(20)-C(19)-Ir(1)	73.6(2)
C(18)-C(19)-Ir(1)	68.3(2)
C(25)-C(19)-Ir(1)	125.3(3)
C(19)-C(20)-C(16)	107.2(3)
C(19)-C(20)-C(23)	127.0(4)
C(16)-C(20)-C(23)	125.8(4)
C(19)-C(20)-Ir(1)	70.1(2)
C(16)-C(20)-Ir(1)	67.15(19)
C(23)-C(20)-Ir(1)	128.9(3)
C(16)-C(21)-H(21A)	109.5
C(16)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(16)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(17)-C(22)-H(22A)	109.5
C(17)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(17)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(18)-C(24)-H(24A)	109.5
C(18)-C(24)-H(24B)	109.5

H(24A)-C(24)-H(24B)	109.5
C(18)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(19)-C(25)-H(25A)	109.5
C(19)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(19)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

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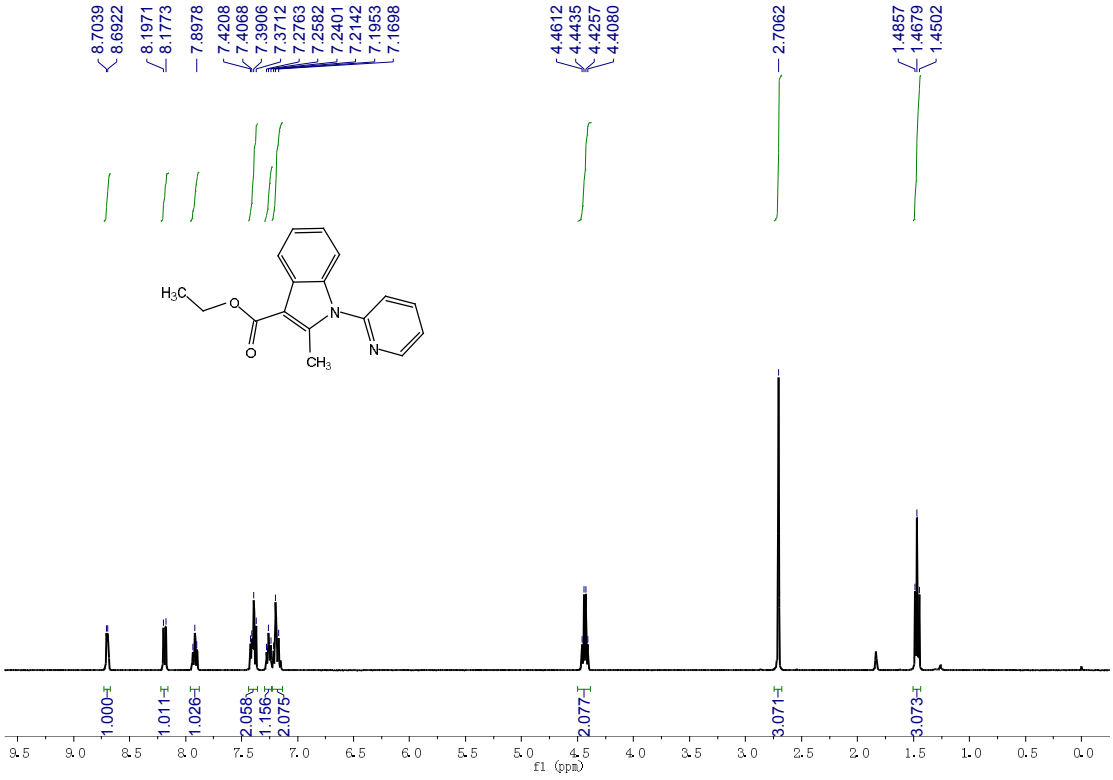
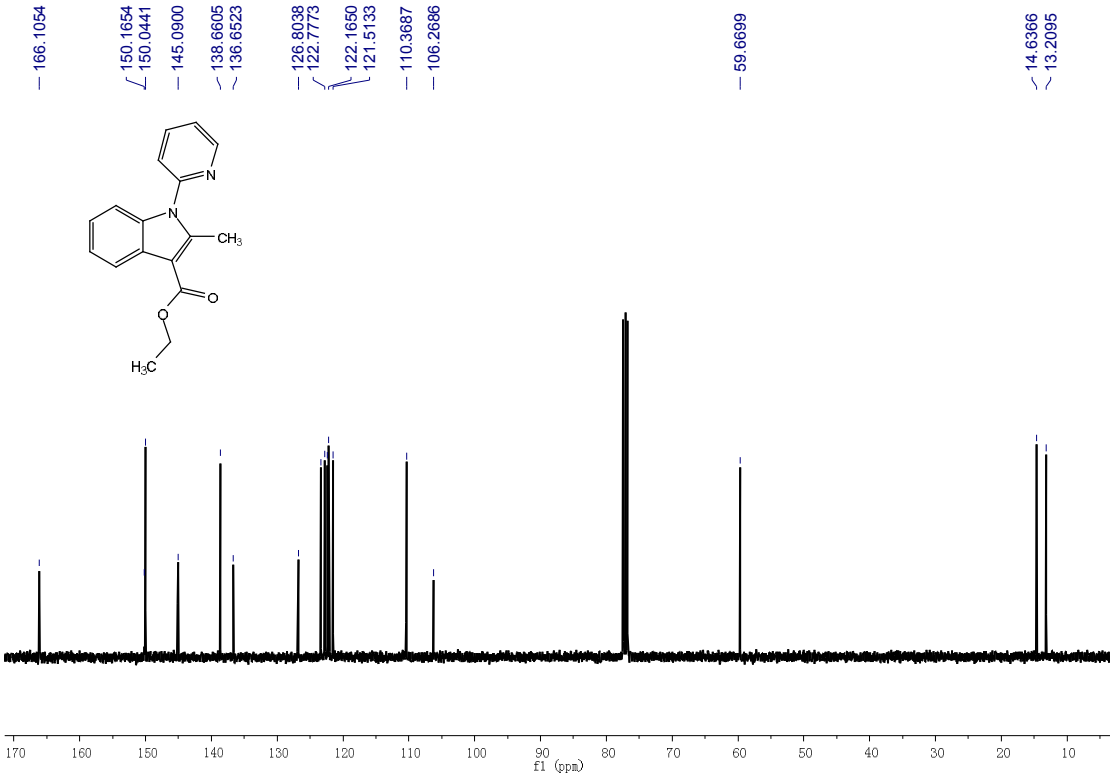
NMR Spectra

3aa





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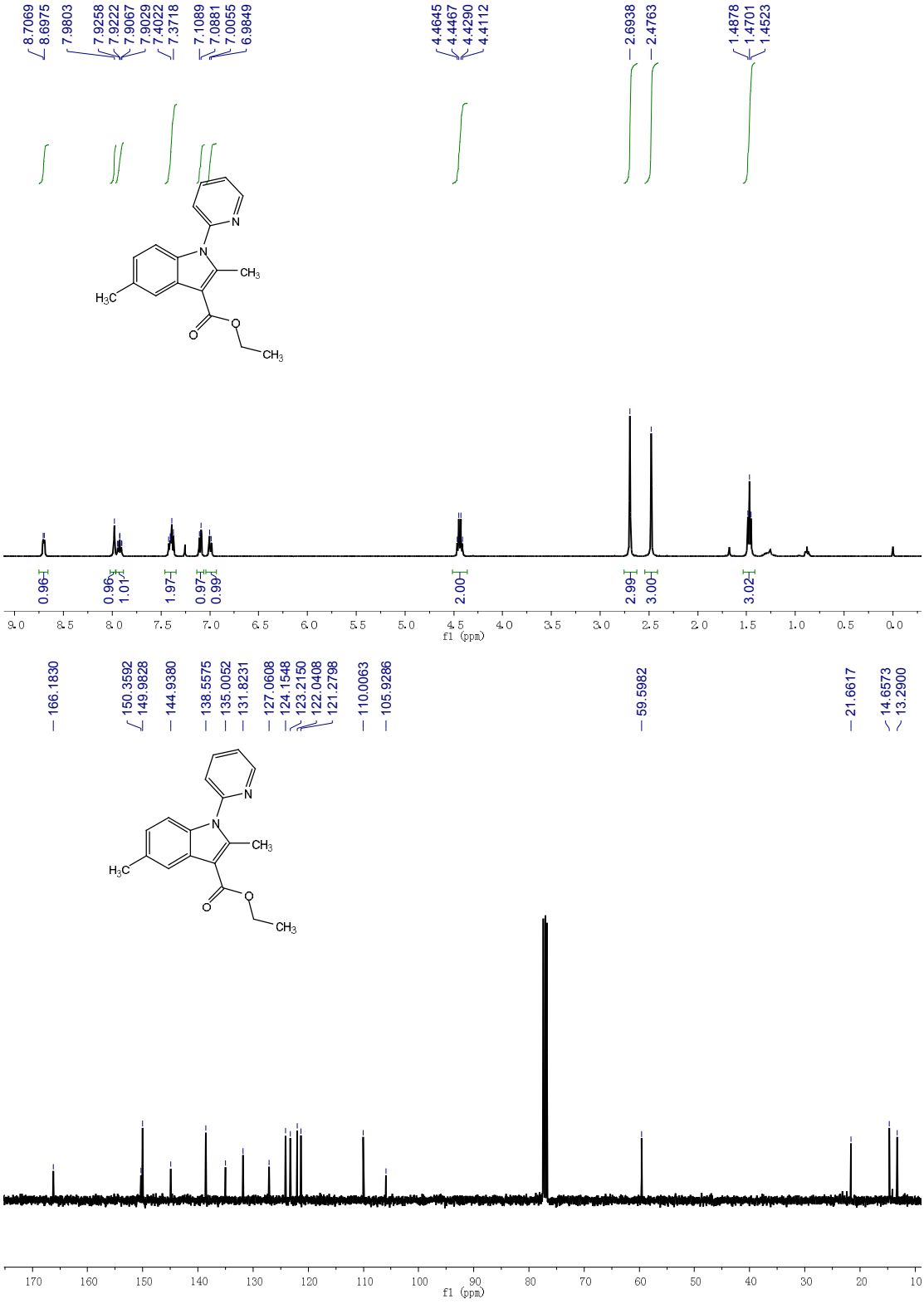
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4.4467
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4.4112
2.6938
2.4763
1.4878
1.4701
1.4523
N
N
CH3
H3C
O
O
CH3
0.96
0.96
1.01
1.97
0.97
0.99
2.00
2.99
3.00
3.02
f1 (ppm)
166.1830
150.3592
149.9828
144.9380
138.5575
135.0052
131.8231
127.0608
124.1548
123.2150
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59.5982
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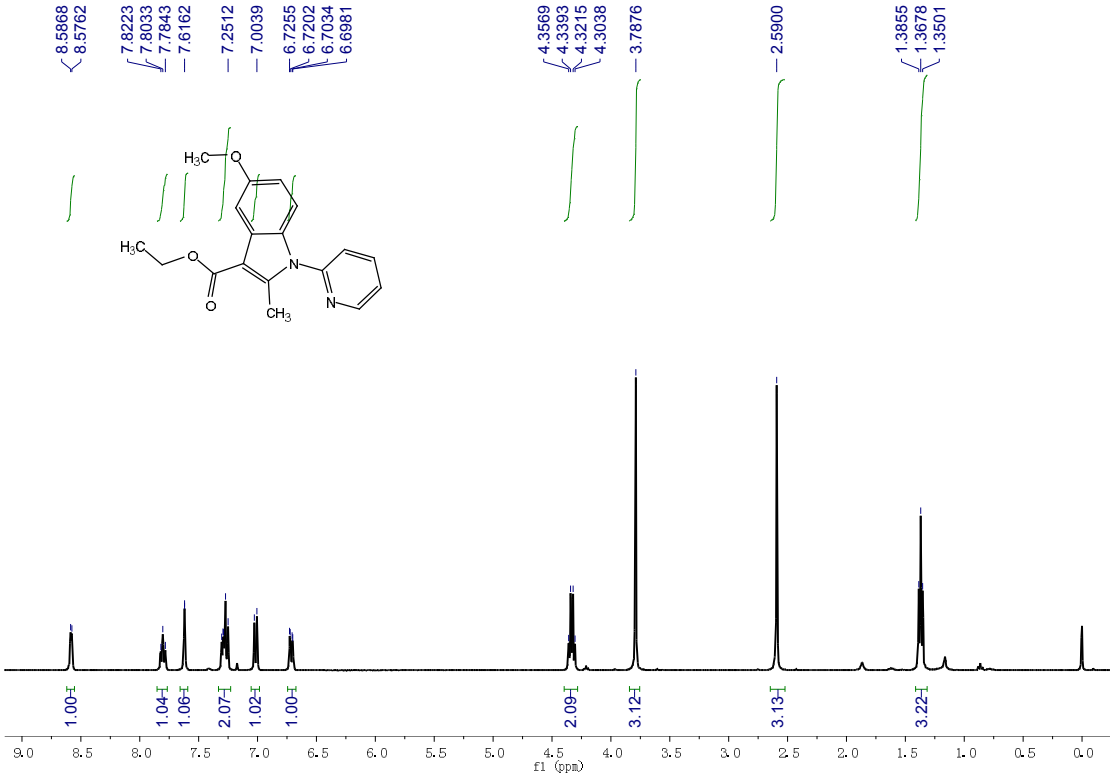
14.6573
13.2900
f1 (ppm)

3ca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6.7034
6.6981
4.3569
4.3393
4.3215
4.3038
3.7876
2.5900
1.3855
1.3678
1.3501
1.00
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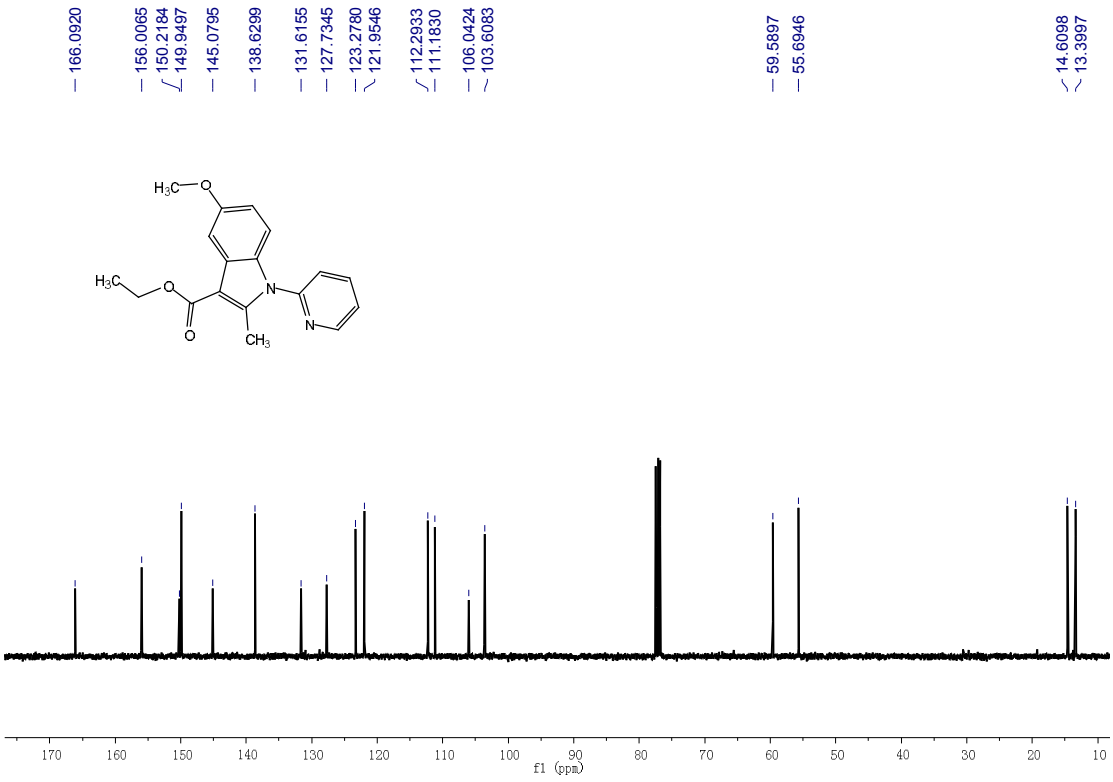
1.06
2.07
1.02
1.00
2.09
3.12
3.13
3.22
f1 (ppm)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59.5897
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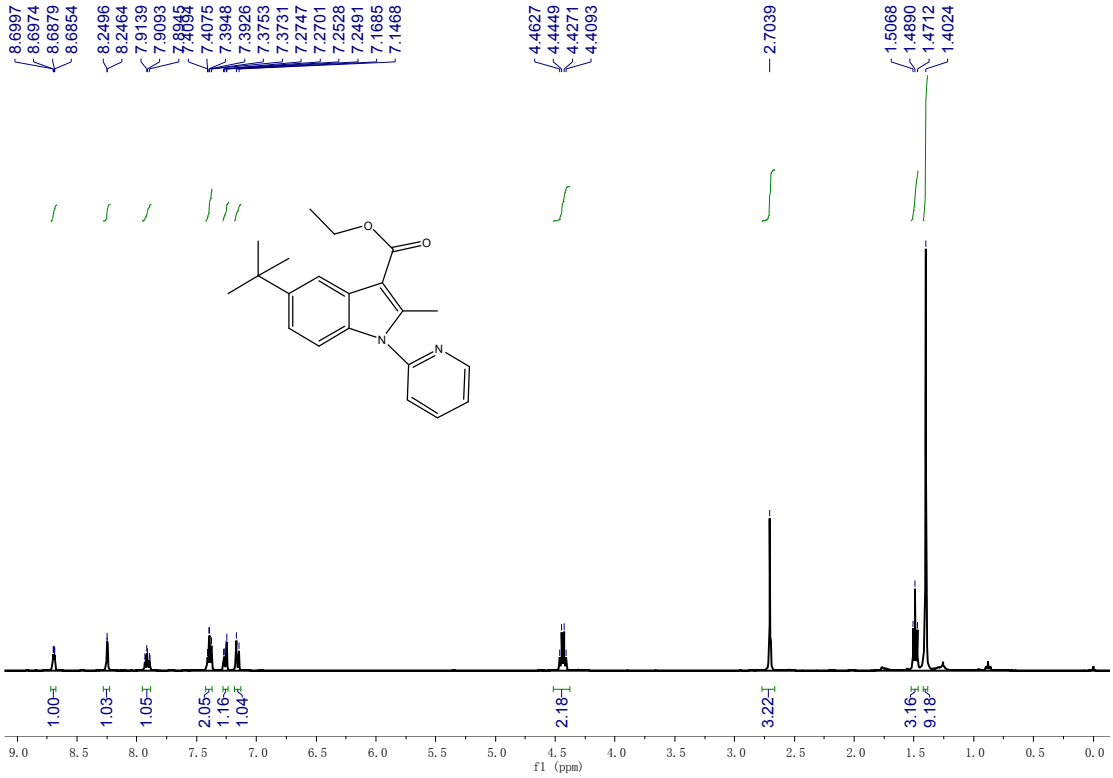
f1 (ppm)

3da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7.3926
7.3753
7.3731
7.2747
7.2701
7.2528
7.2491
7.1685
7.1468
4.4627
4.4449
4.4271
4.4093
2.7039
1.5068
1.4890
1.4712
1.4024
1.00
1.03
1.05
2.05
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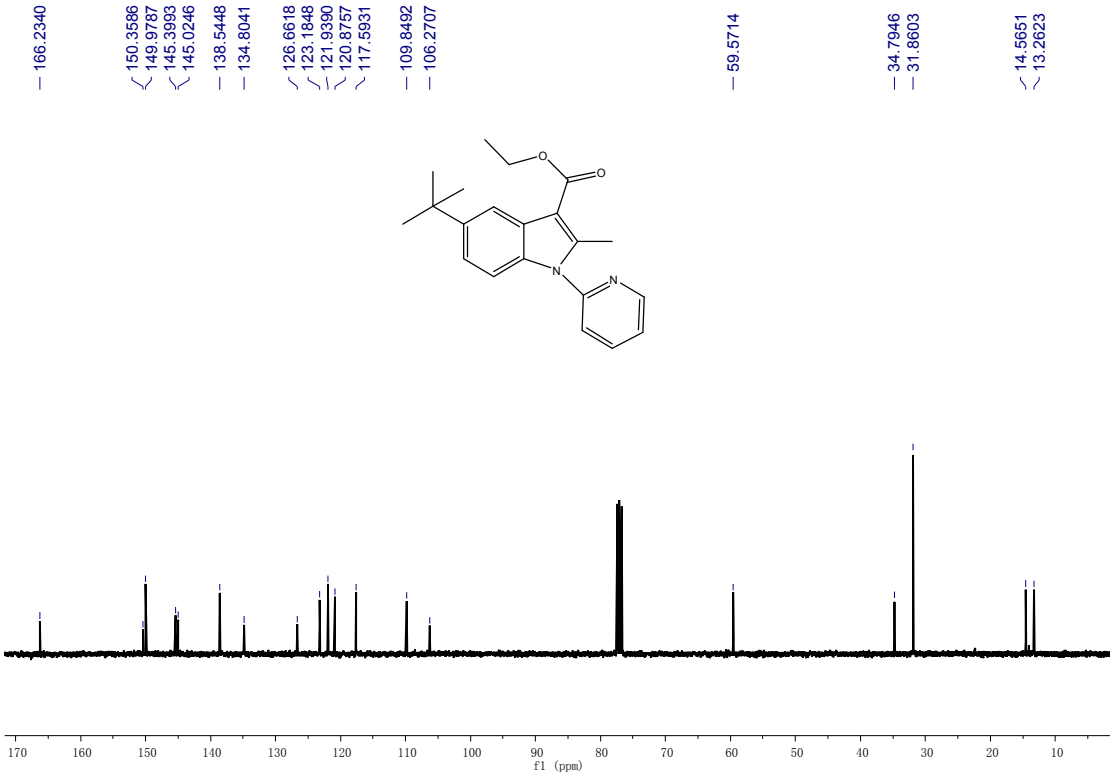
2.18
3.22
3.16
9.18
f1 (ppm)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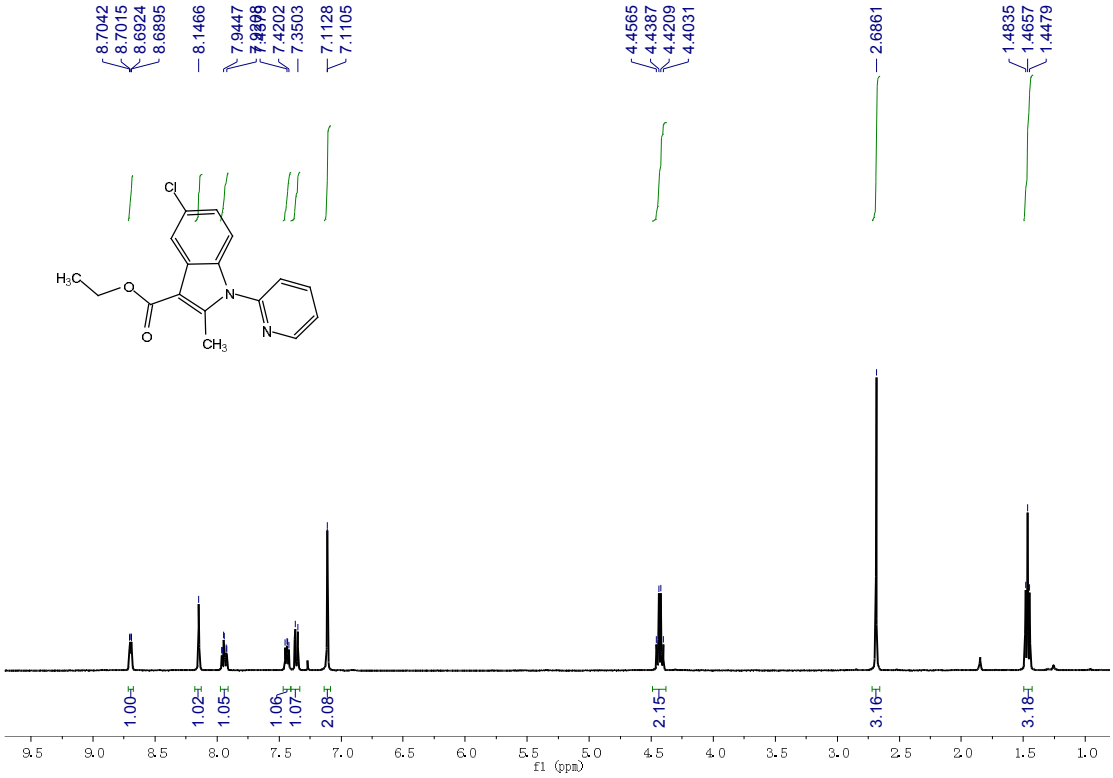
f1 (ppm)

3ea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4.4209
4.4031
2.6861
1.4835
1.4657
1.4479
Cl
H3C
O
O
N
N
CH3
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1.06
1.07
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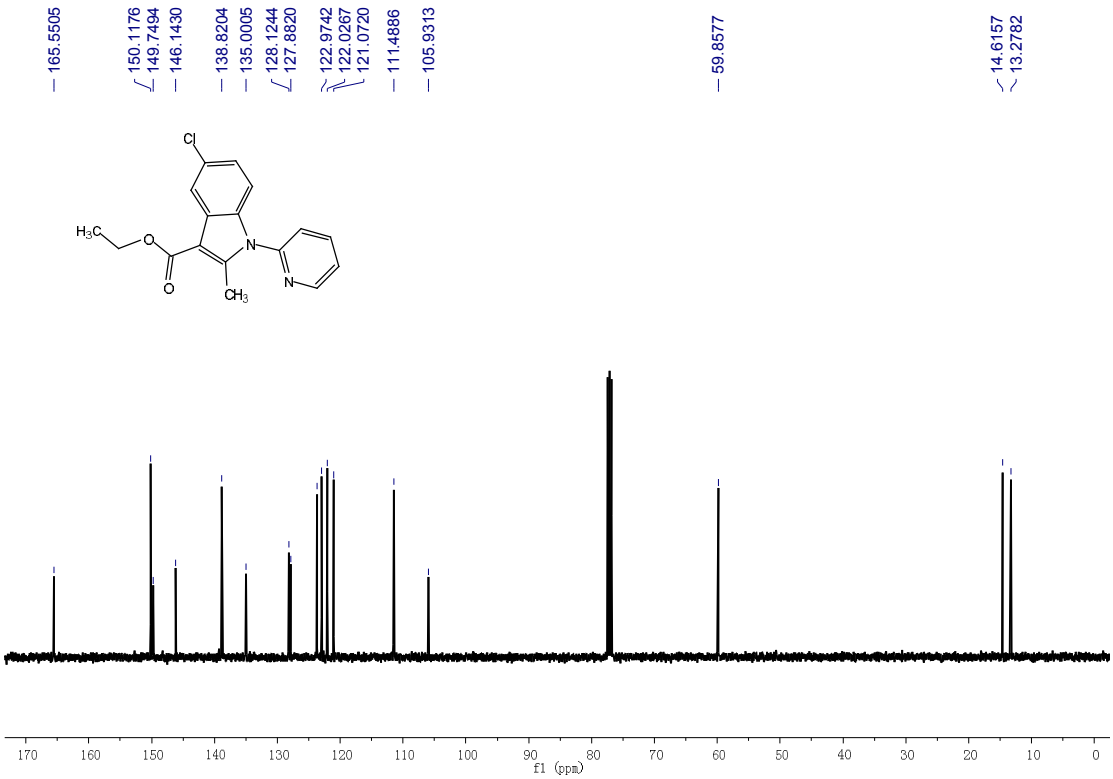
2.15
3.16
3.18
f1 (ppm)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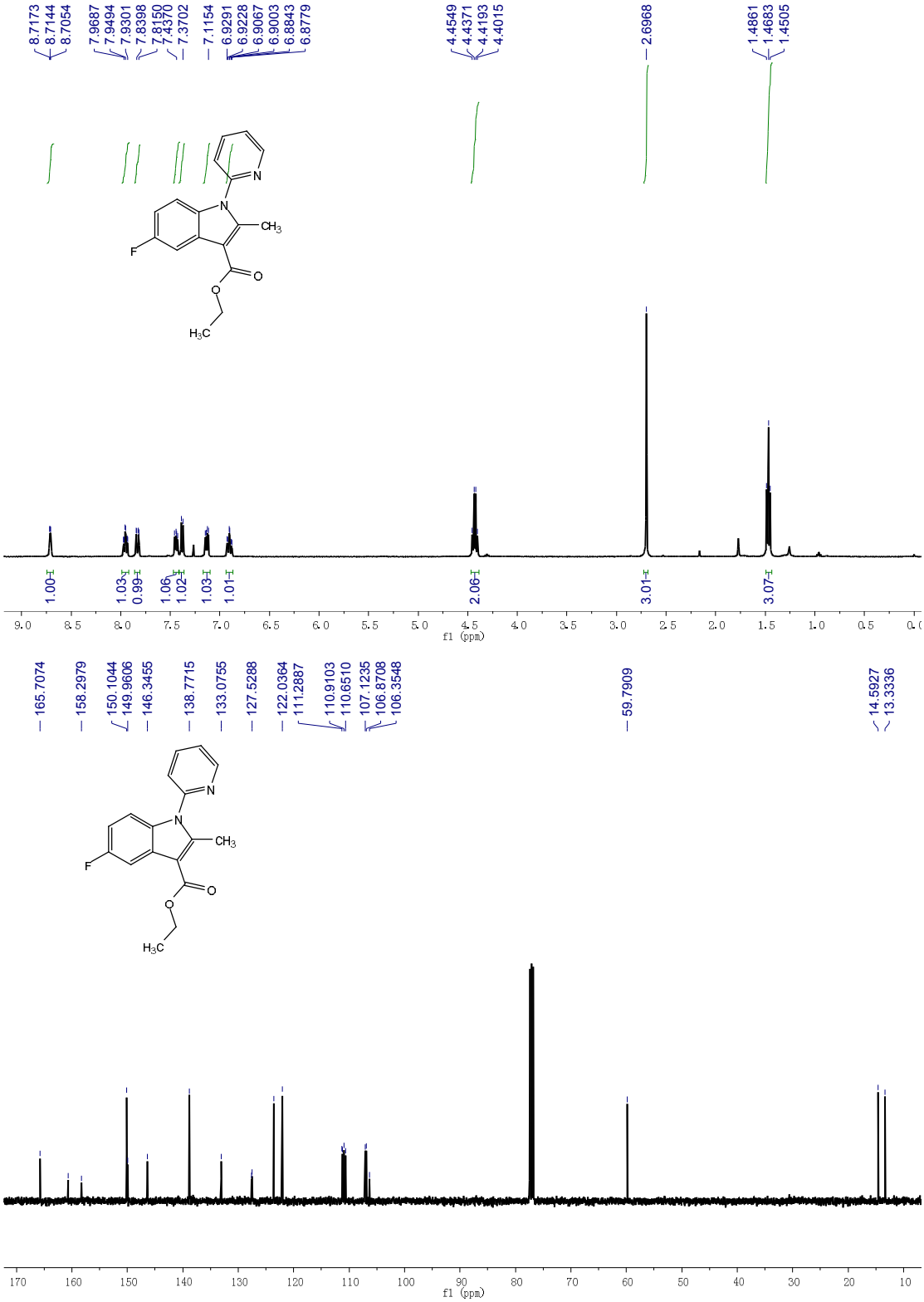
Cl
H3C
O
O
N
N
CH3
f1 (ppm)

3fa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6.9067
6.9003
6.8843
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1.4861
1.4683
1.4505
N
N
CH3
F
O
O
H3C
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1.03
0.99
1.06
1.02
1.03
1.01
2.06
3.01
3.07
f1 (ppm)
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158.2979
150.1044
149.9606
146.3455
138.7715
133.0755
127.5288
122.0364
111.2887
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107.1235
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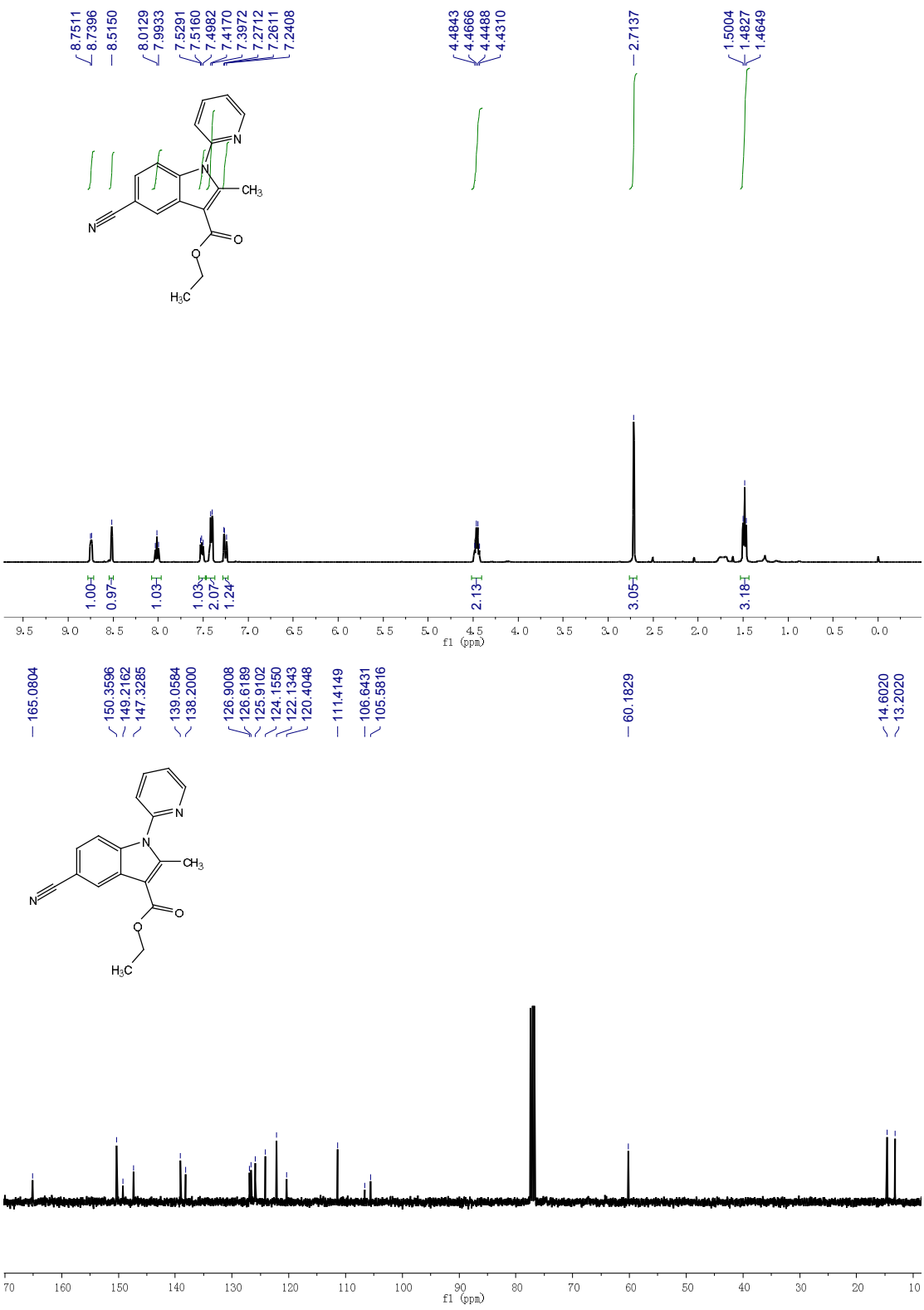
14.5927
13.3336
f1 (ppm)

3ga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7.4170
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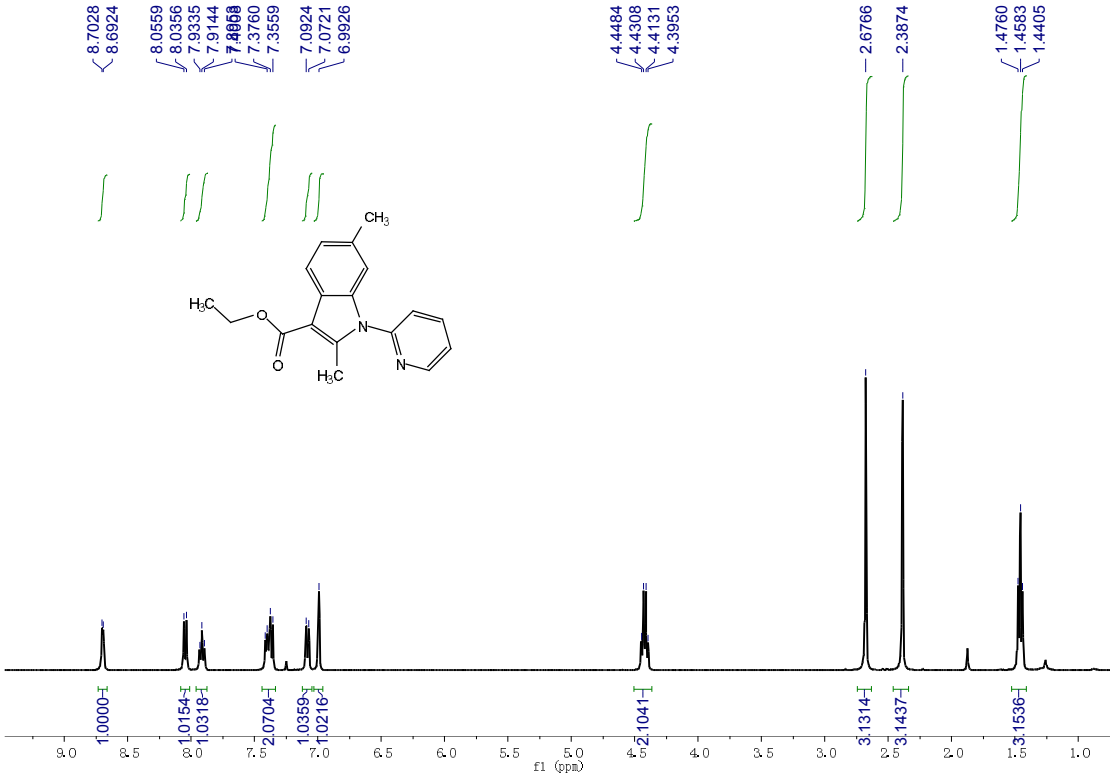
7.2712
7.2611
7.2408
4.4843
4.4666
4.4488
4.4310
2.7137
1.5004
1.4827
1.4649
1.00
0.97
1.03
1.03
2.07
1.24
2.13
3.05
3.18
f1 (ppm)
165.0804
150.3596
149.2162
147.3285
139.0584
138.2000
126.9008
126.6189
125.9102
124.1550
122.1343
120.4048
111.4149
106.6431
105.5816
60.1829
14.6020
13.2020
f1 (ppm)

3ha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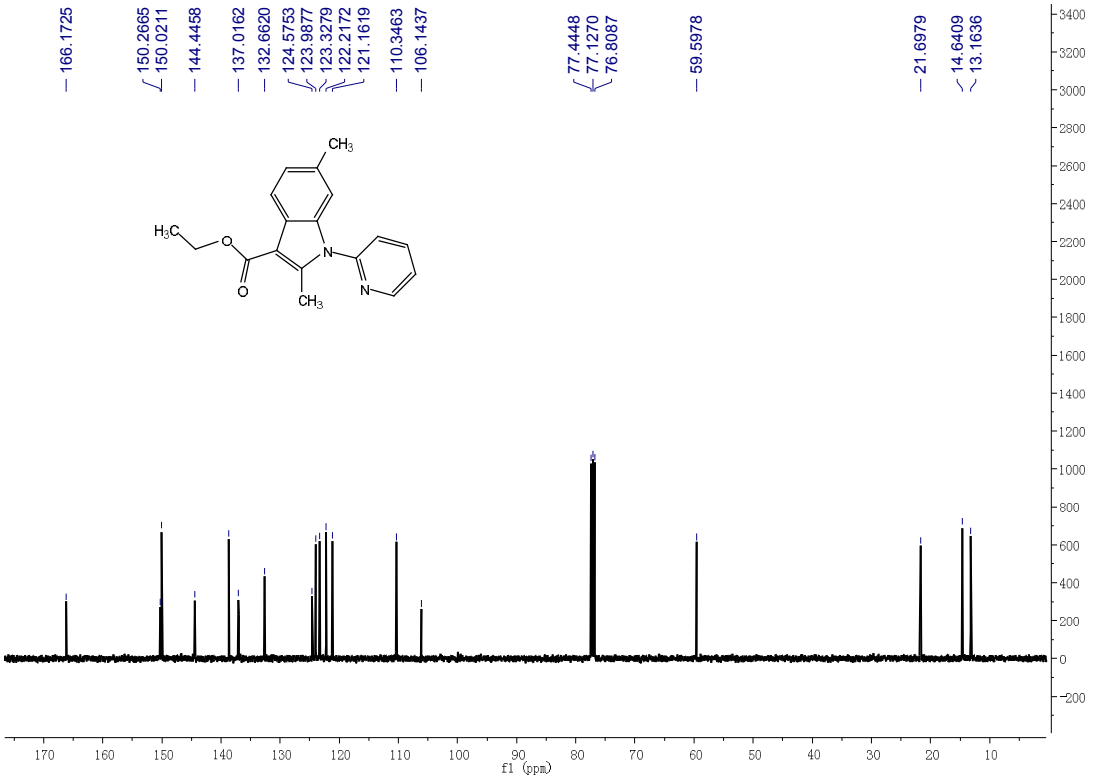
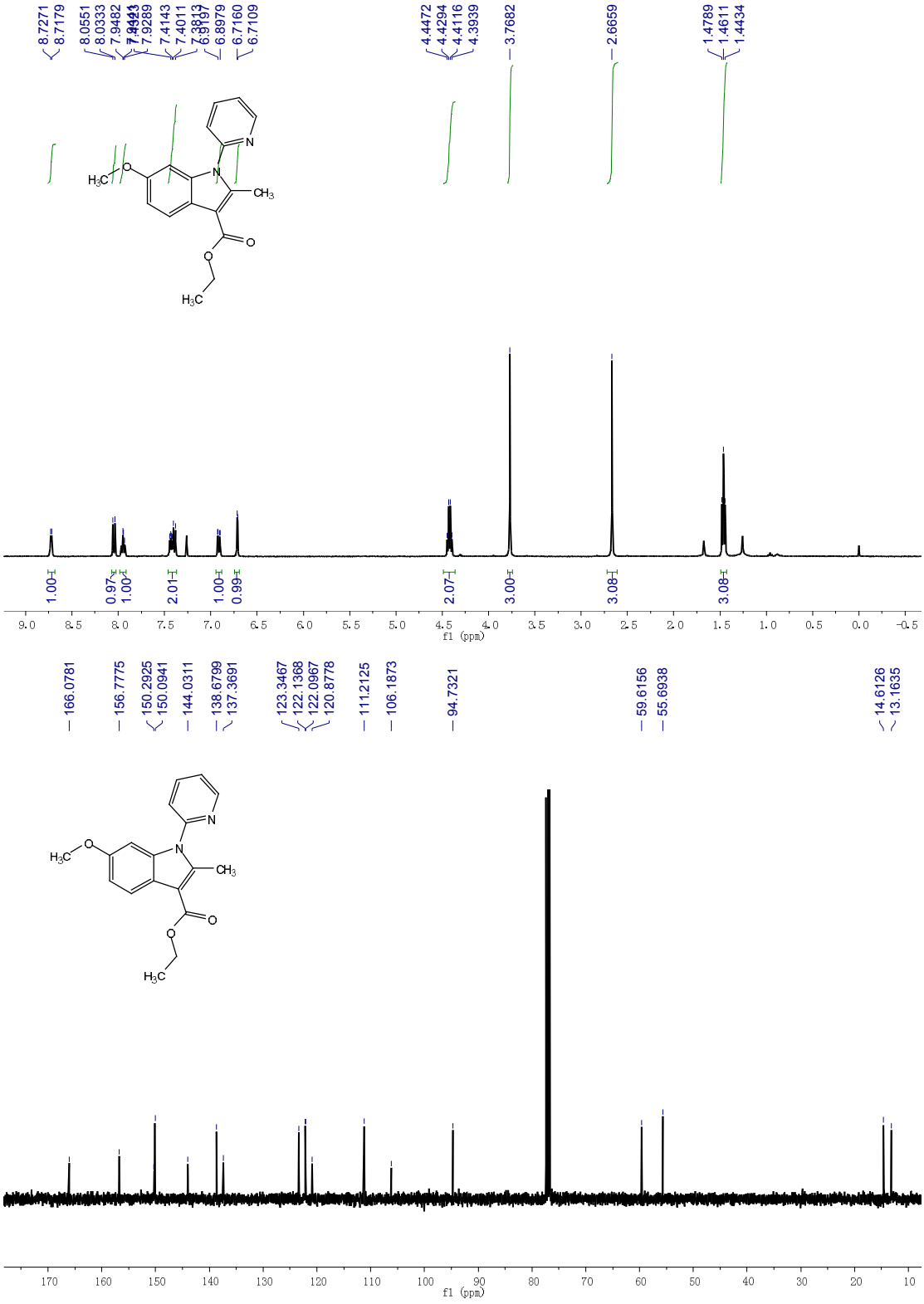
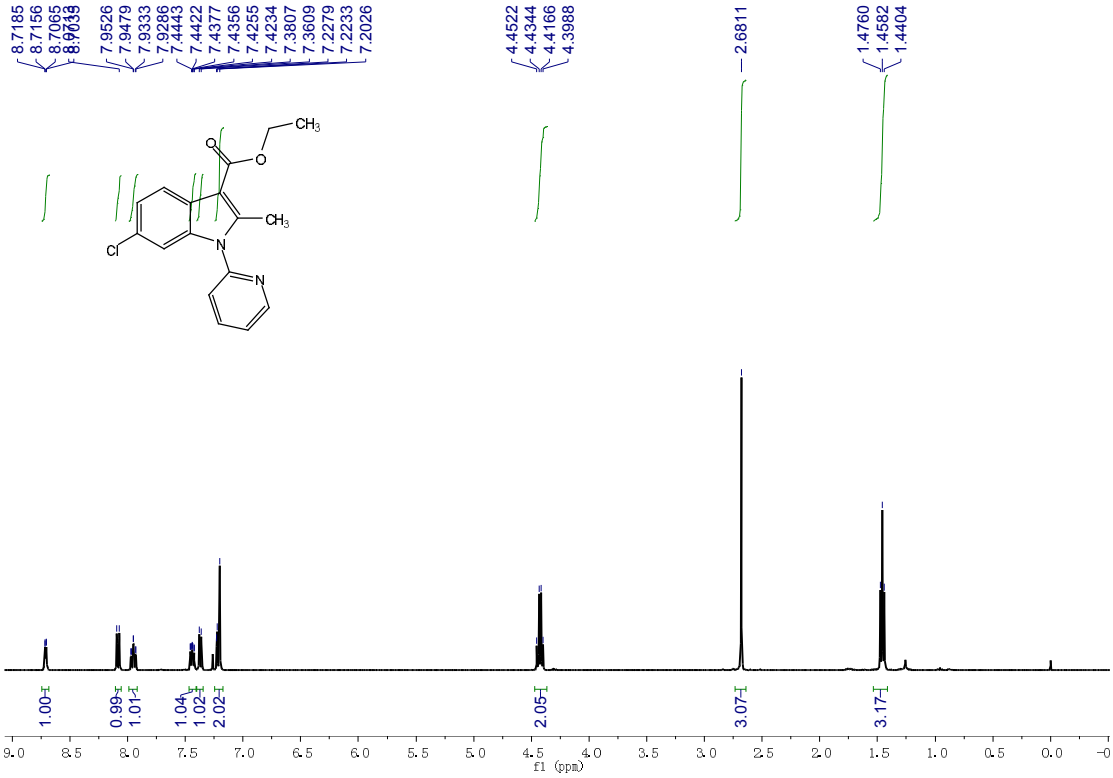
8.6924
8.0559
8.0356
7.9335
7.9144
7.3760
7.3559
7.0924
7.0721
6.9926
4.4484
4.4308
4.4131
4.3953
2.6766
2.3874
1.4760
1.4583
1.4405
CH3
H3C
O
N
N
H3C
1.0000
1.0154
1.0318
2.0704
1.0359
1.0216
2.1041
3.1314
3.1437
3.1536
f1 (ppm)

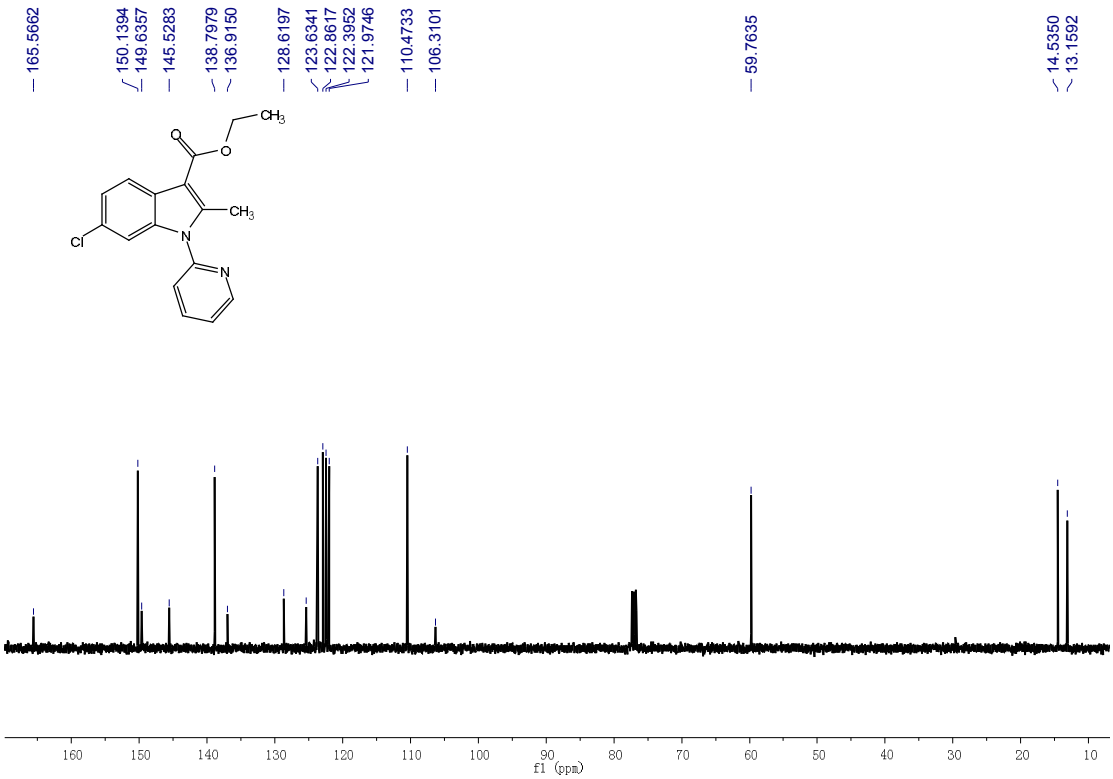

166.1725
150.2665
150.0211
144.4458
137.0162
132.6620
124.5753
123.9877
123.3279
122.2172
121.1619
110.3463
106.1437
77.4448
77.1270
76.8087
59.5978
21.6979
14.6409
13.1636
CH3
H3C
O
N
N
CH3
f1 (ppm)

3ia

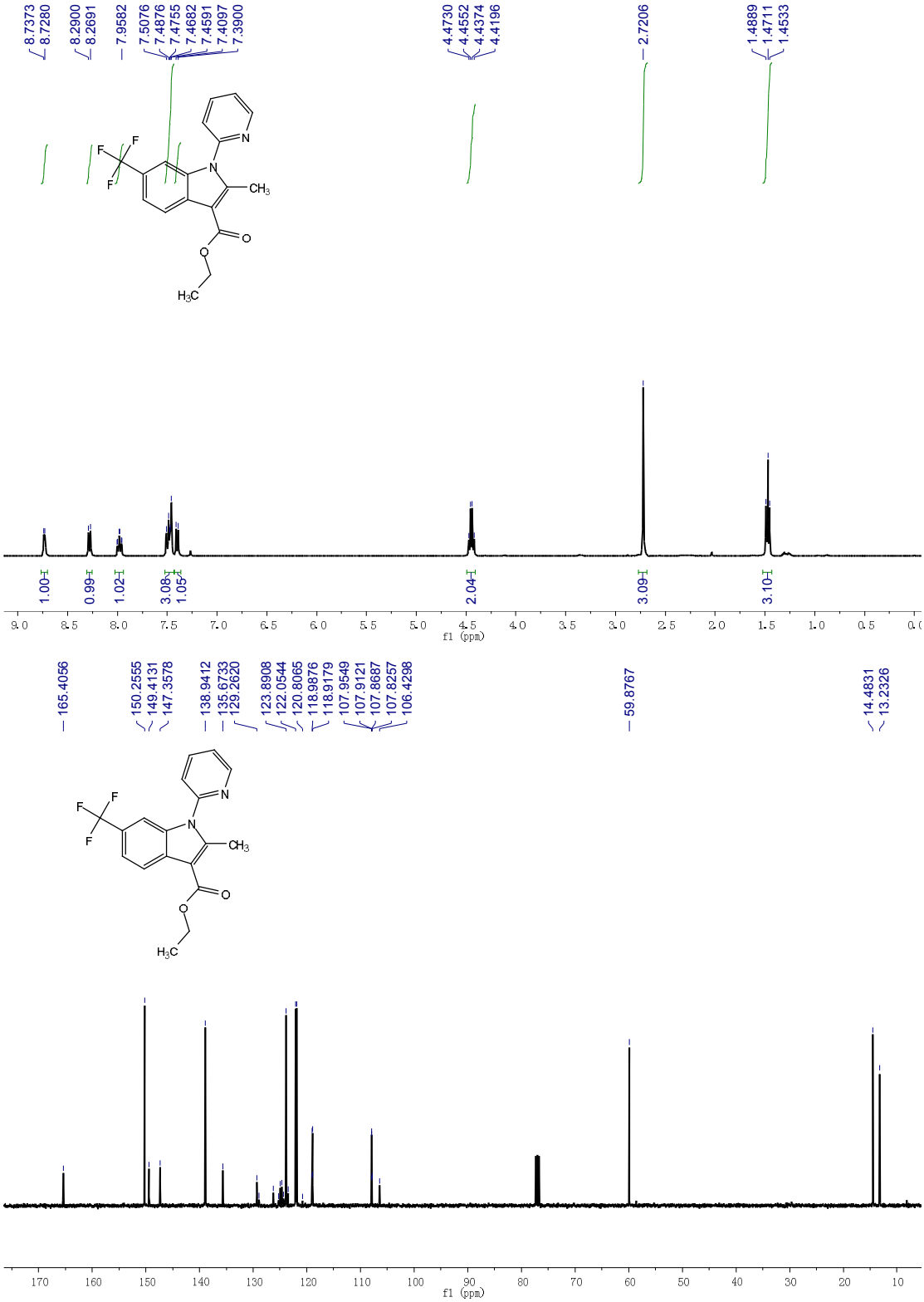

8.7271
8.7179
8.0551
8.0333
7.9482
7.9289
7.4143
7.4011
7.3813
6.8979
6.7160
6.7109
4.4472
4.4294
4.4116
4.3939
3.7682
2.6659
1.4789
1.4611
1.4434
1.00
0.97
1.00
2.01
1.00
0.99
2.07
3.00
3.08
3.08
f1 (ppm)
166.0781
156.7775
150.2925
150.0941
144.0311
138.6799
137.3691
123.3467
122.1368
122.0967
120.8778
111.2125
106.1873
94.7321
59.6156
55.6938
14.6126
13.1635
f1 (ppm)

3ja

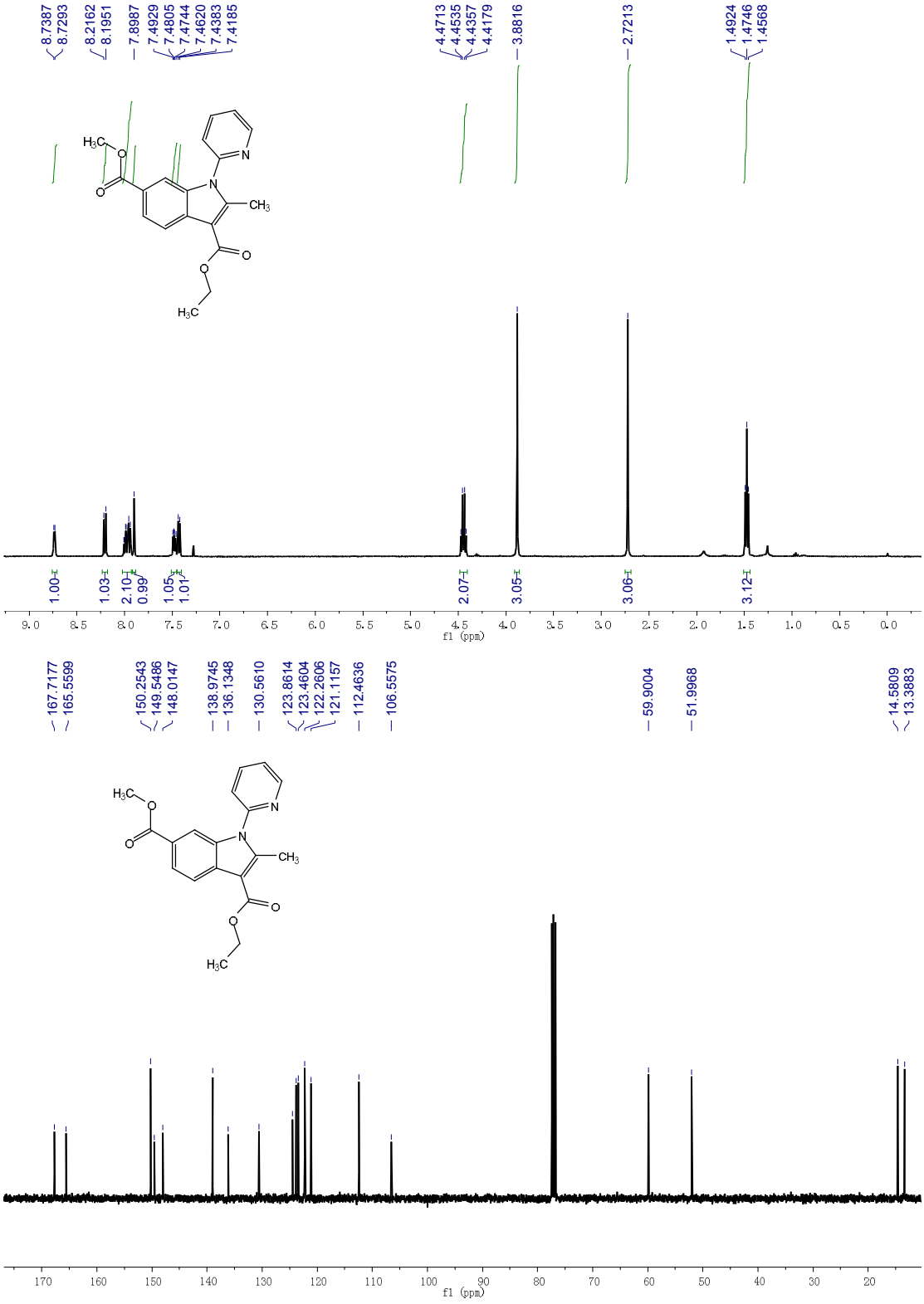

8.7185
8.7156
8.7065
7.9526
7.9479
7.9333
7.9286
7.4443
7.4422
7.4377
7.4356
7.4255
7.4234
7.3807
7.3609
7.2279
7.2233
7.2026
4.4522
4.4344
4.4166
4.3988
2.6811
1.4760
1.4582
1.4404
CH3
O
O
CH3
Cl
N
N
1.00
0.99
1.01
1.04
1.02
2.02
2.05
3.07
3.17
f1 (ppm)


165.5662
150.1394
149.6357
145.5283
138.7979
136.9150
128.6197
123.6341
122.8617
122.3952
121.9746
110.4733
106.3101
59.7635
14.5350
13.1592
CH3
O
O
CH3
Cl
N
N
f1 (ppm)

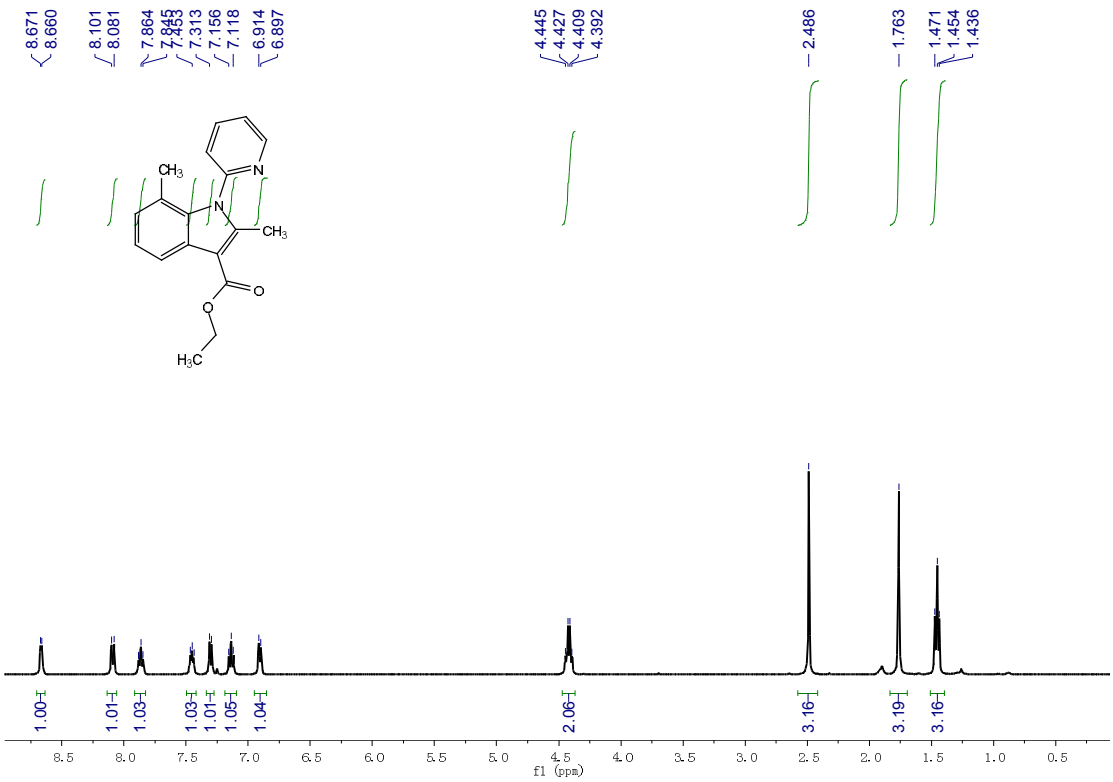
3ka

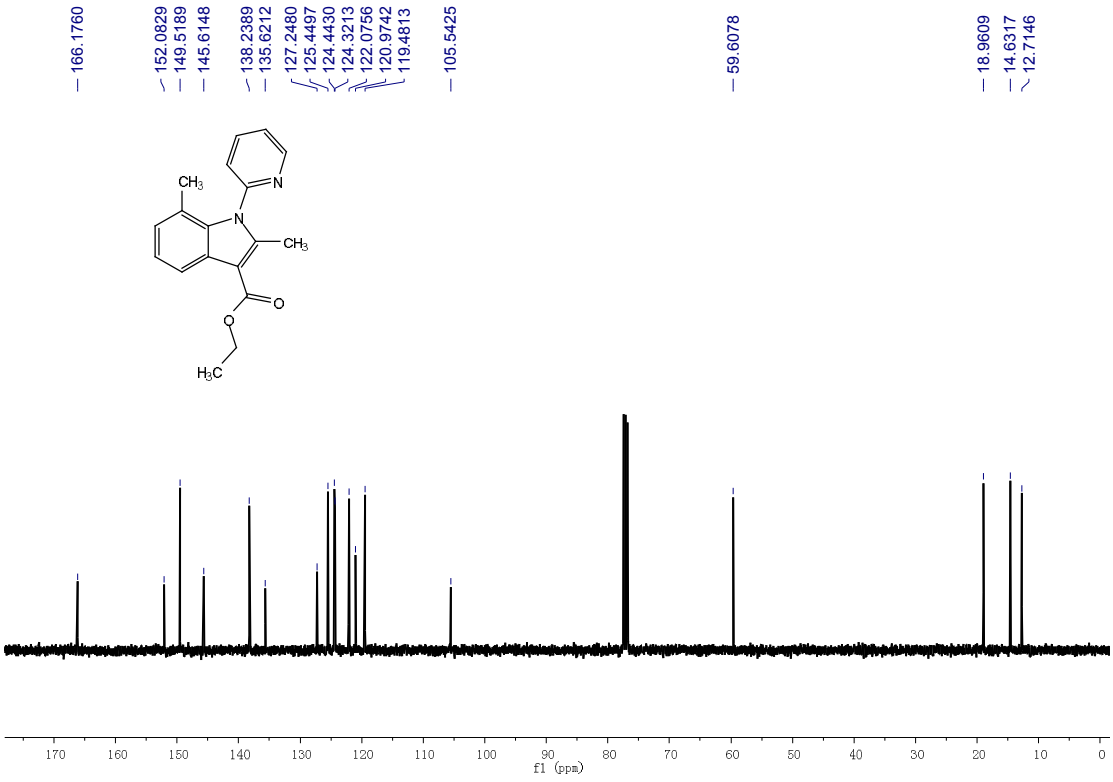

8.7373
8.7280
8.2900
8.2691
7.9582
7.5076
7.4876
7.4755
7.4682
7.4591
7.4097
7.3900
4.4730
4.4552
4.4374
4.4196
2.7206
1.4889
1.4711
1.4533
1.00
0.99
1.02
3.08
1.05
2.04
3.09
3.10
f1 (ppm)
165.4056
150.2555
149.4131
147.3578
138.9412
135.6733
129.2620
123.8908
122.0544
120.8065
118.9876
118.9179
107.9549
107.9121
107.8687
107.8257
106.4298
59.8767
14.4831
13.2326
f1 (ppm)

3la

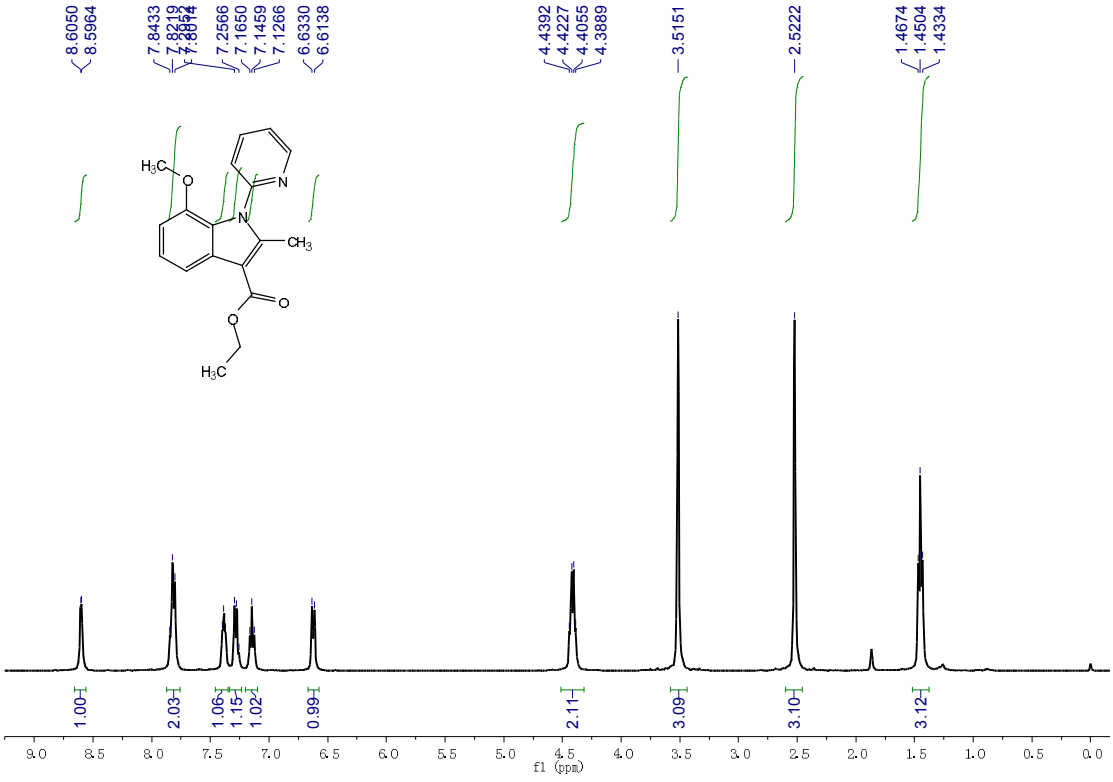

8.7387
8.7293
8.2162
8.1951
7.8987
7.4929
7.4805
7.4744
7.4620
7.4383
7.4185
4.4713
4.4535
4.4357
4.4179
3.8816
2.7213
1.4924
1.4746
1.4568
1.00
1.03
2.10
0.99
1.05
1.01
2.07
3.05
3.06
3.12
f1 (ppm)
167.7177
165.5599
150.2543
149.5486
148.0147
138.9745
136.1348
130.5610
123.8614
123.4604
122.2606
121.1157
112.4636
106.5575
59.9004
51.9968
14.5809
13.3883
f1 (ppm)

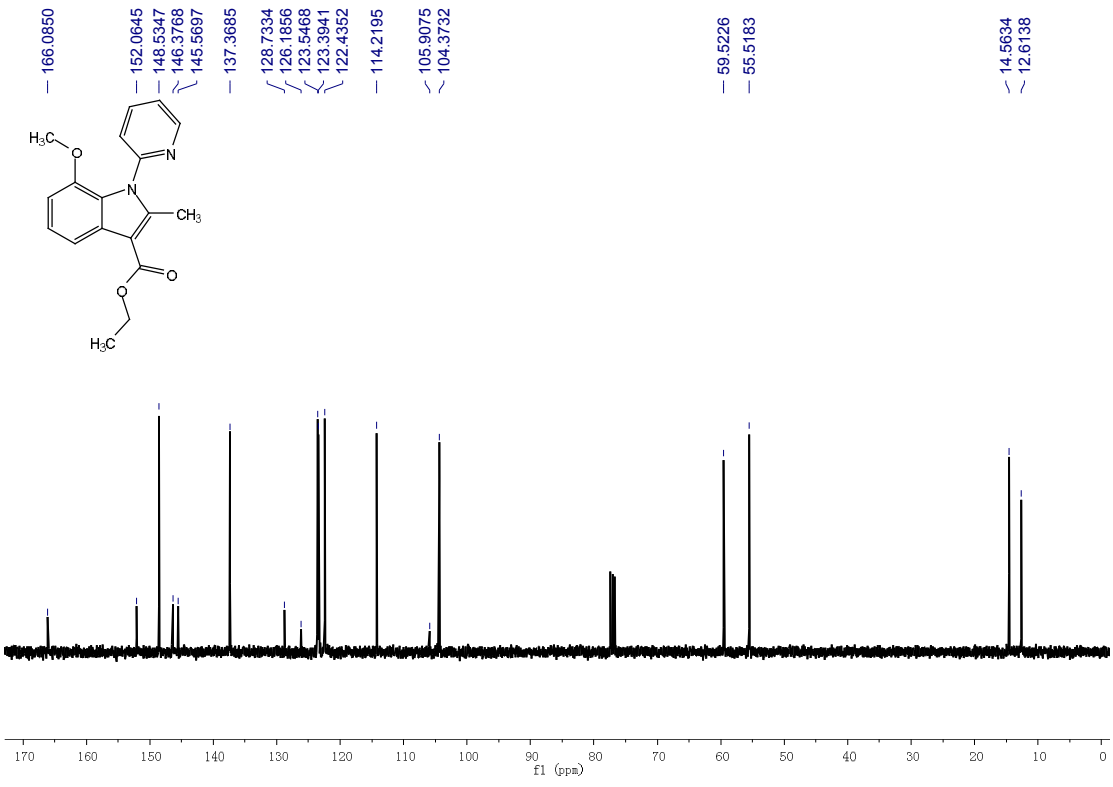
3ma


8.671
8.660
8.101
8.081
7.864
7.845
7.453
7.313
7.156
7.118
6.914
6.897
4.445
4.427
4.409
4.392
2.486
1.763
1.471
1.454
1.436
CH3
N
N
CH3
O
O
H3C
1.00
1.01
1.03
1.03
1.01
1.05
1.04
2.06
3.16
3.19
3.16
f1 (ppm)


166.1760
152.0829
149.5189
145.6148
138.2389
135.6212
127.2480
125.4497
124.4430
124.3213
122.0756
120.9742
119.4813
105.5425
59.6078
18.9609
14.6317
12.7146
CH3
N
N
CH3
O
O
H3C
f1 (ppm)

3na


8.6050
8.5964
7.8433
7.8219
7.8014
7.2566
7.1650
7.1459
7.1266
6.6330
6.6138
4.4392
4.4227
4.4055
4.3889
3.5151
2.5222
1.4674
1.4504
1.4334
1.00
2.03
1.06
1.15
1.02
0.99
2.11
3.09
3.10
3.12
f1 (ppm)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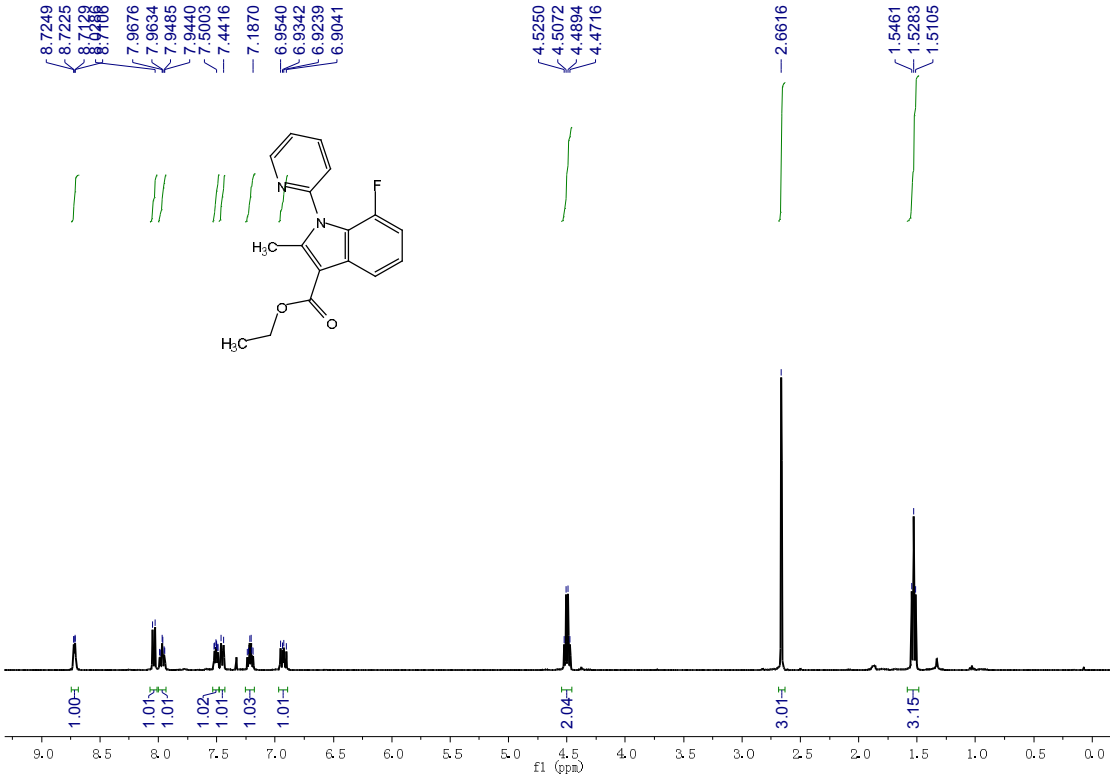
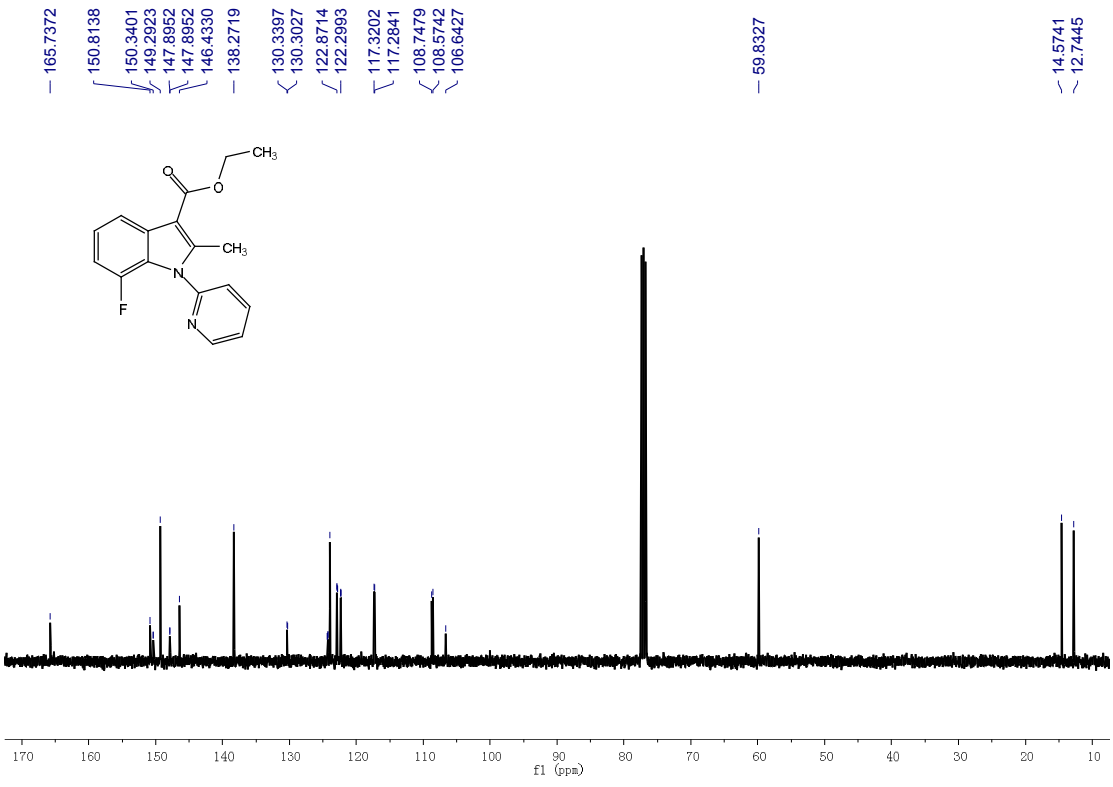
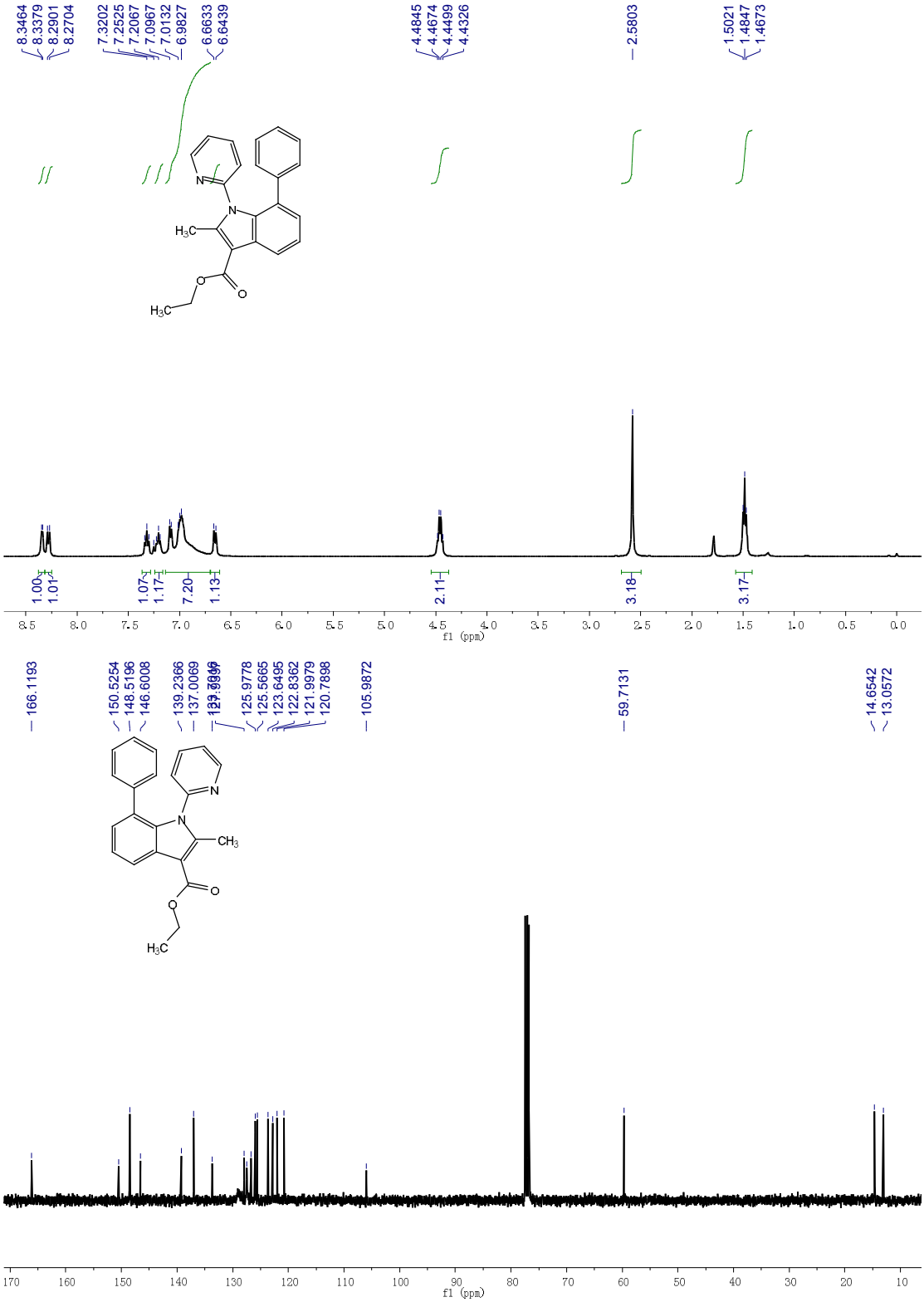
152.0645
148.5347
146.3768
145.5697
137.3685
128.7334
126.1856
123.5468
123.3941
122.4352
114.2195
105.9075
104.3732
59.5226
55.5183
14.5634
12.6138
f1 (ppm)

3oa

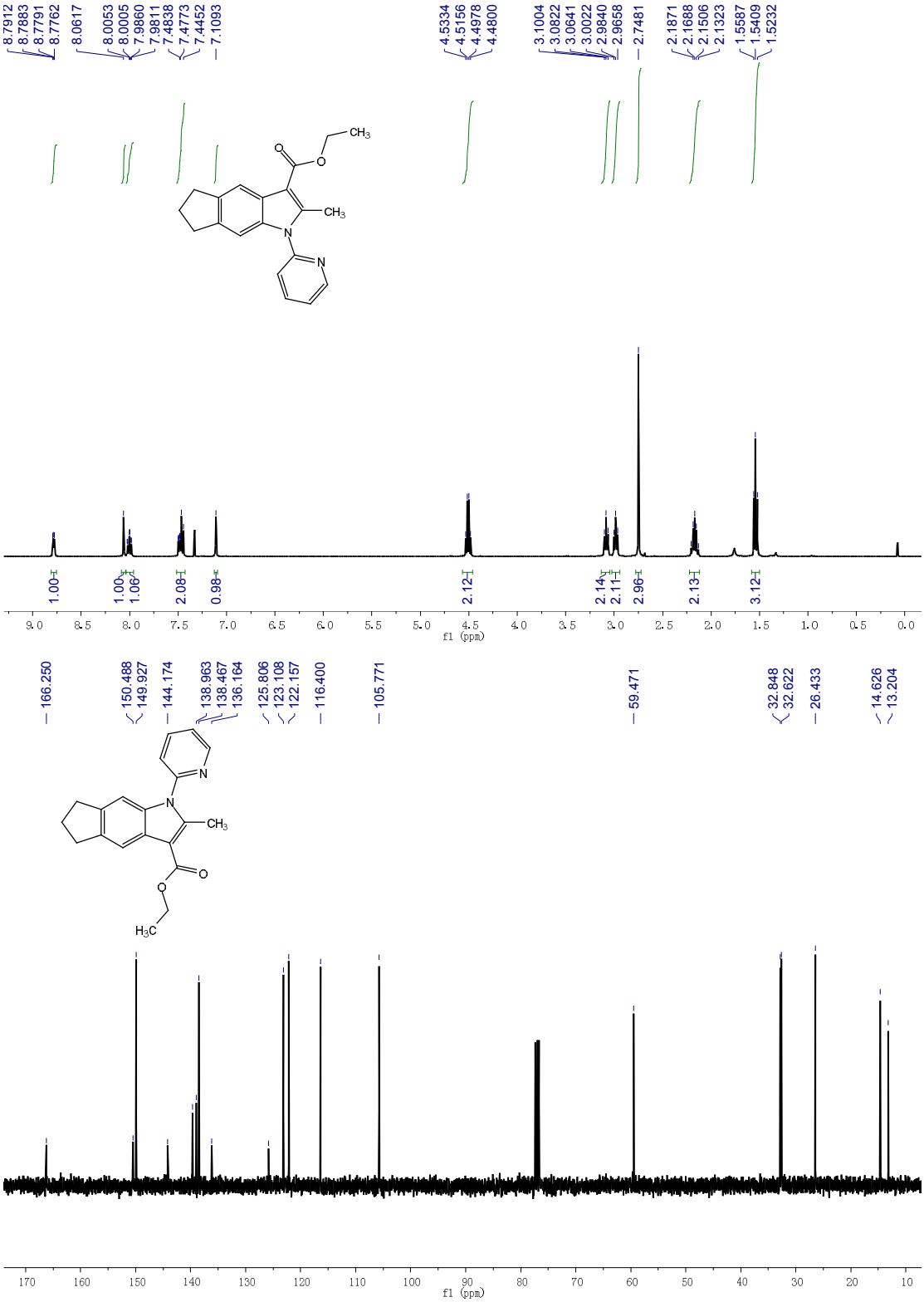

8.7249
8.7225
7.9676
7.9634
7.9485
7.9440
7.5003
7.4416
7.1870
6.9540
6.9342
6.9239
6.9041
4.5250
4.5072
4.4894
4.4716
2.6616
1.5461
1.5283
1.5105
F
N
H3C
O
O
H3C
1.00
1.01
1.01
1.02
1.01
1.03
1.01
2.04
3.01
3.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.7372
150.8138
150.3401
149.2923
147.8952
147.8952
146.4330
138.2719
130.3397
130.3027
122.8714
122.2993
117.3202
117.2841
108.7479
108.5742
106.6427
59.8327
14.5741
12.7445
CH3
O
O
CH3
N
F
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3pa


8.3464
8.3379
8.2901
8.2704
7.3202
7.2525
7.2067
7.0967
7.0132
6.9827
6.6633
6.6439
4.4845
4.4674
4.4499
4.4326
2.5803
1.5021
1.4847
1.4673
N
N
H3C
O
O
H3C
1.00
1.01
1.07
1.17
7.20
1.13
2.11
3.18
3.17
f1 (ppm)
166.1193
150.5254
148.5196
146.6008
139.2366
137.0069
125.9778
125.5665
123.6495
122.8362
121.9979
120.7898
105.9872
59.7131
14.6542
13.0572
N
N
CH3
O
O
H3C
f1 (ppm)

3qa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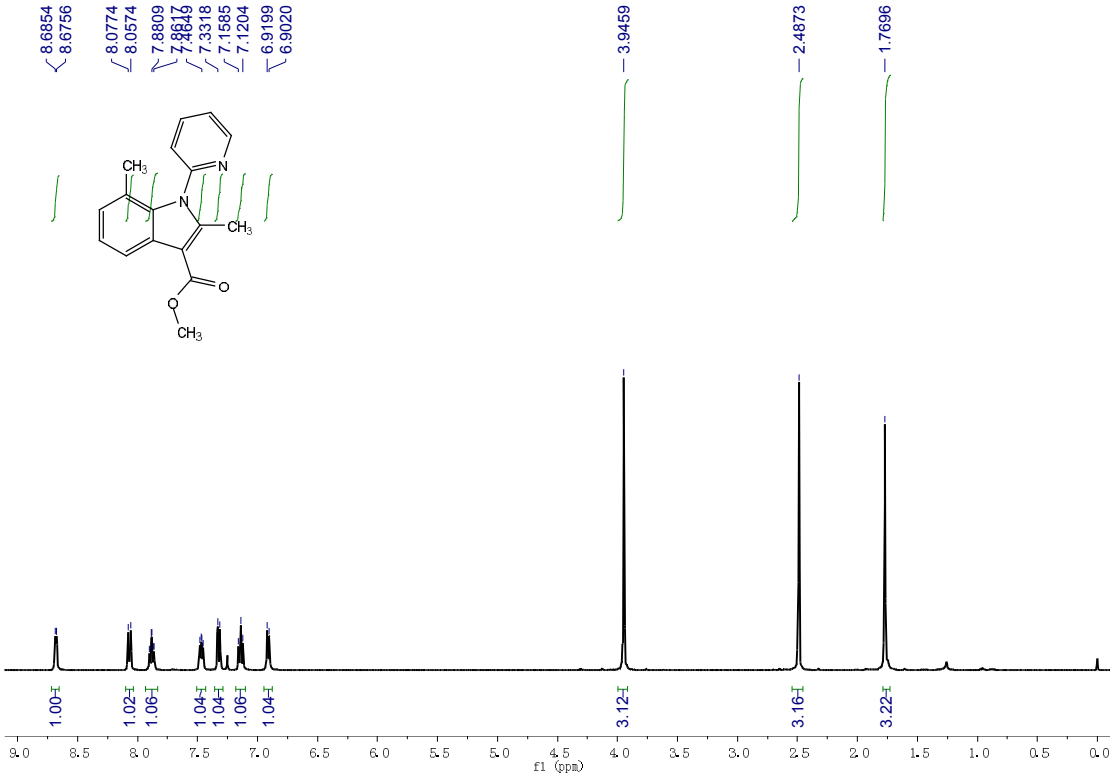
8.7791
8.7762
8.0617
8.0053
8.0005
7.9860
7.9811
7.4838
7.4773
7.4452
7.1093
4.5334
4.5156
4.4978
4.4800
3.1004
3.0822
3.0641
3.0022
2.9840
2.9658
2.7481
2.1871
2.1688
2.1506
2.1323
1.5587
1.5409
1.5232
CH3
O
O
CH3
N
N
1.00
1.00
1.06
2.08
0.98
2.12
2.14
2.11
2.96
2.13
3.12
f1 (ppm)
166.250
150.488
149.927
144.174
138.963
138.467
136.164
125.806
123.108
122.157
116.400
105.771
59.471
32.848
32.622
26.433
14.626
13.204
N
N
CH3
O
O
H3C
f1 (ppm)

3mb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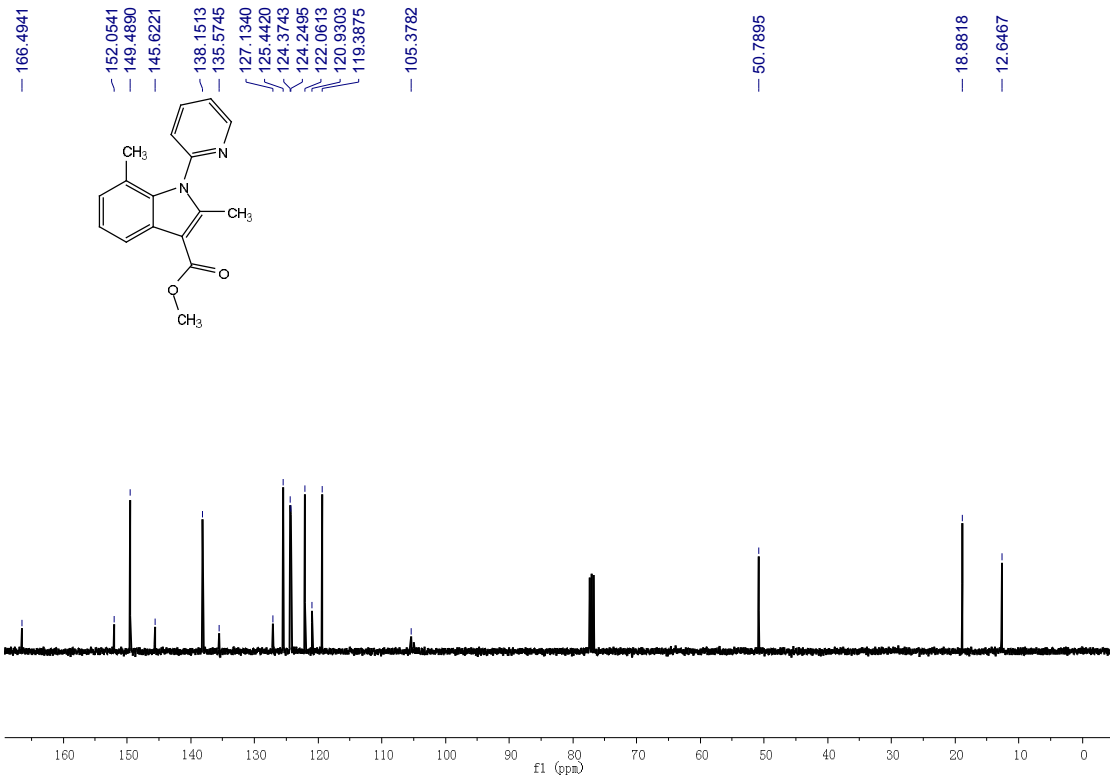
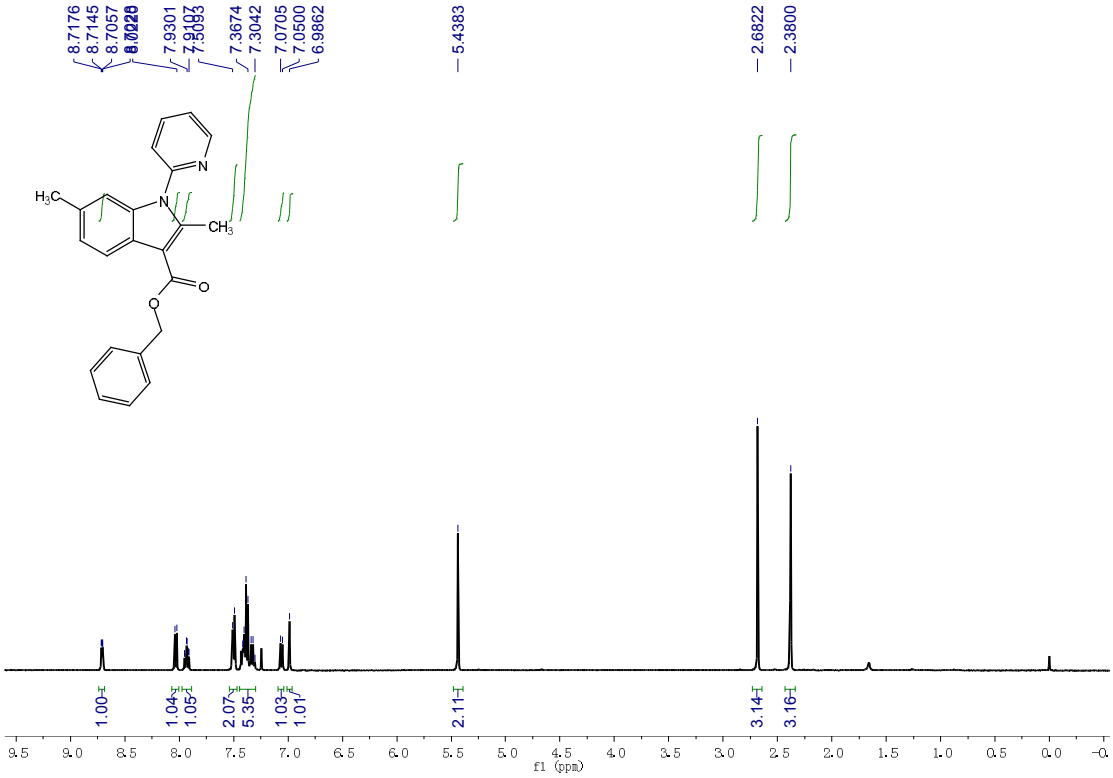
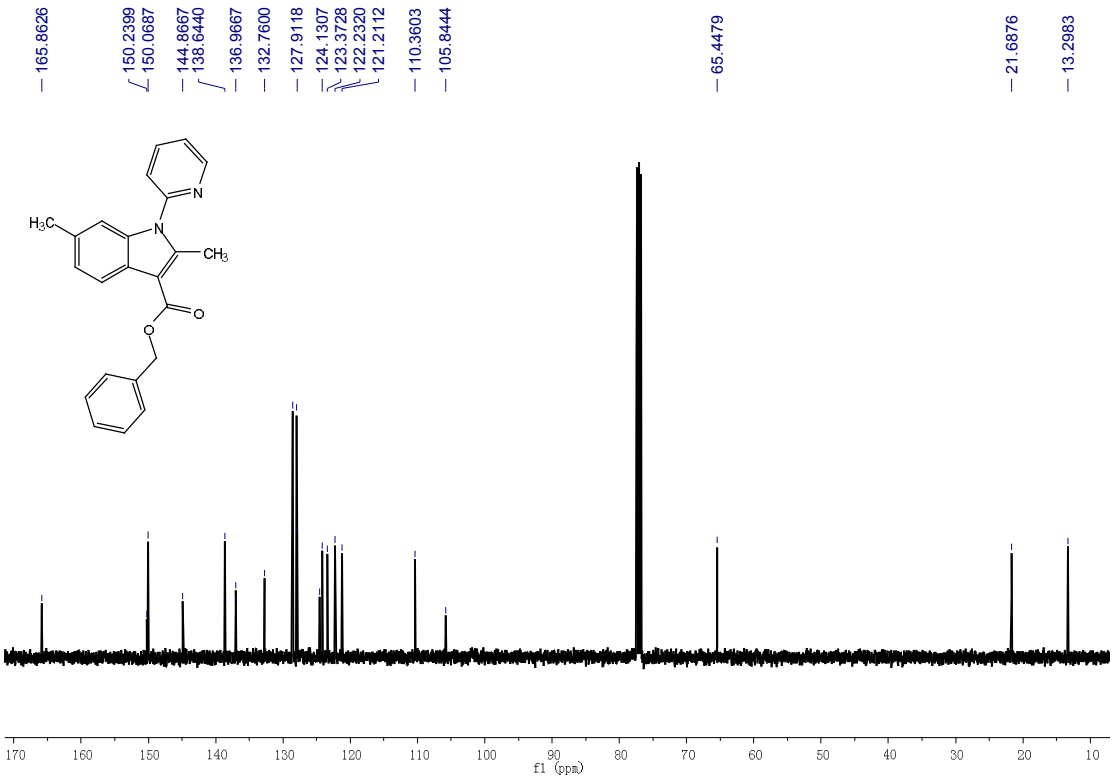
8.0774
8.0574
7.8809
7.8617
7.4649
7.3318
7.1585
7.1204
6.9199
6.9020
3.9459
2.4873
1.7696
1.00
1.02
1.06
1.04
1.04
1.06
1.04
3.12
3.16
3.22
f1 (ppm)

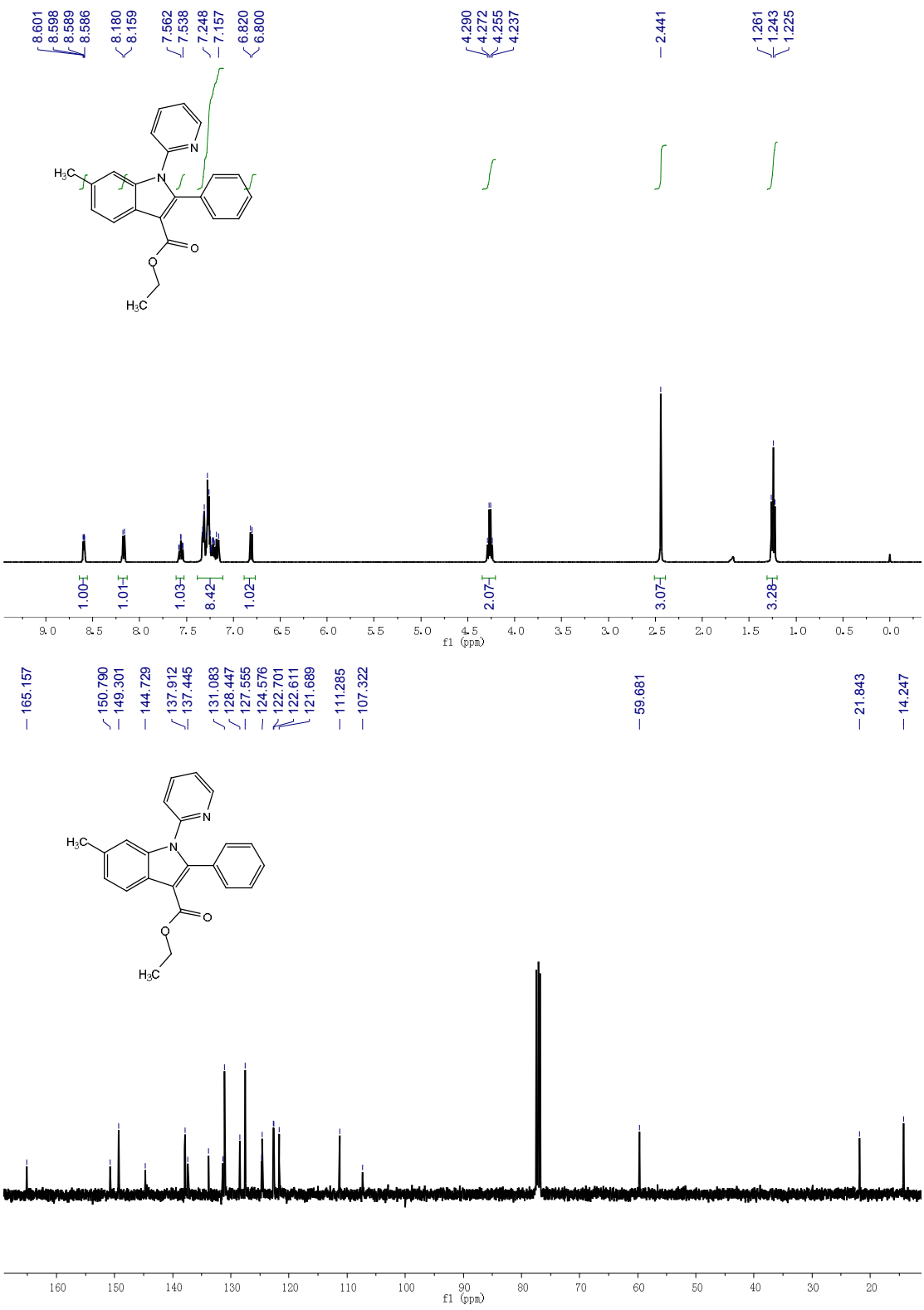

166.4941
152.0541
149.4890
145.6221
138.1513
135.5745
127.1340
125.4420
124.3743
124.2495
122.0613
120.9303
119.3875
105.3782
50.7895
18.8818
12.6467
f1 (ppm)

3hc

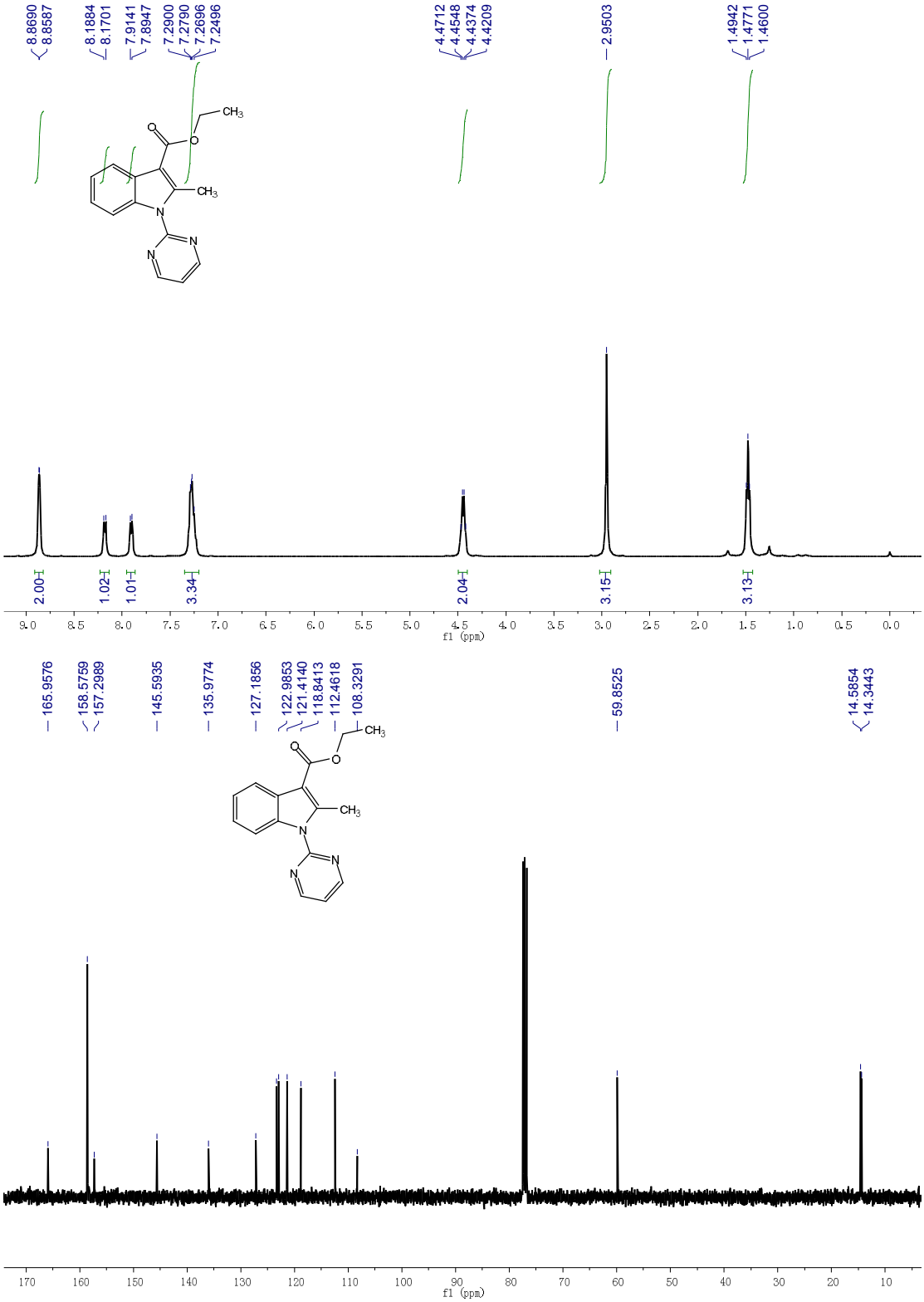

8.7176
8.7145
8.7057
7.9301
7.3674
7.3042
7.0705
7.0500
6.9862
5.4383
2.6822
2.3800
1.00
1.04
1.05
2.07
5.35
1.03
1.01
2.11
3.14
3.16
f1 (ppm)


165.8626
150.2399
150.0687
144.8667
138.6440
136.9667
132.7600
127.9118
124.1307
123.3728
122.2320
121.2112
110.3603
105.8444
65.4479
21.6876
13.2983
f1 (ppm)

3hd


8.601
8.598
8.589
8.586
8.180
8.159
7.562
7.538
7.248
7.157
6.820
6.800
4.290
4.272
4.255
4.237
2.441
1.261
1.243
1.225
1.00
1.01
1.03
8.42
1.02
2.07
3.07
3.28
f1 (ppm)
165.157
150.790
149.301
144.729
137.912
137.445
131.083
128.447
127.555
124.576
122.701
122.611
121.689
111.285
107.322
59.681
21.843
14.247
f1 (ppm)

3ra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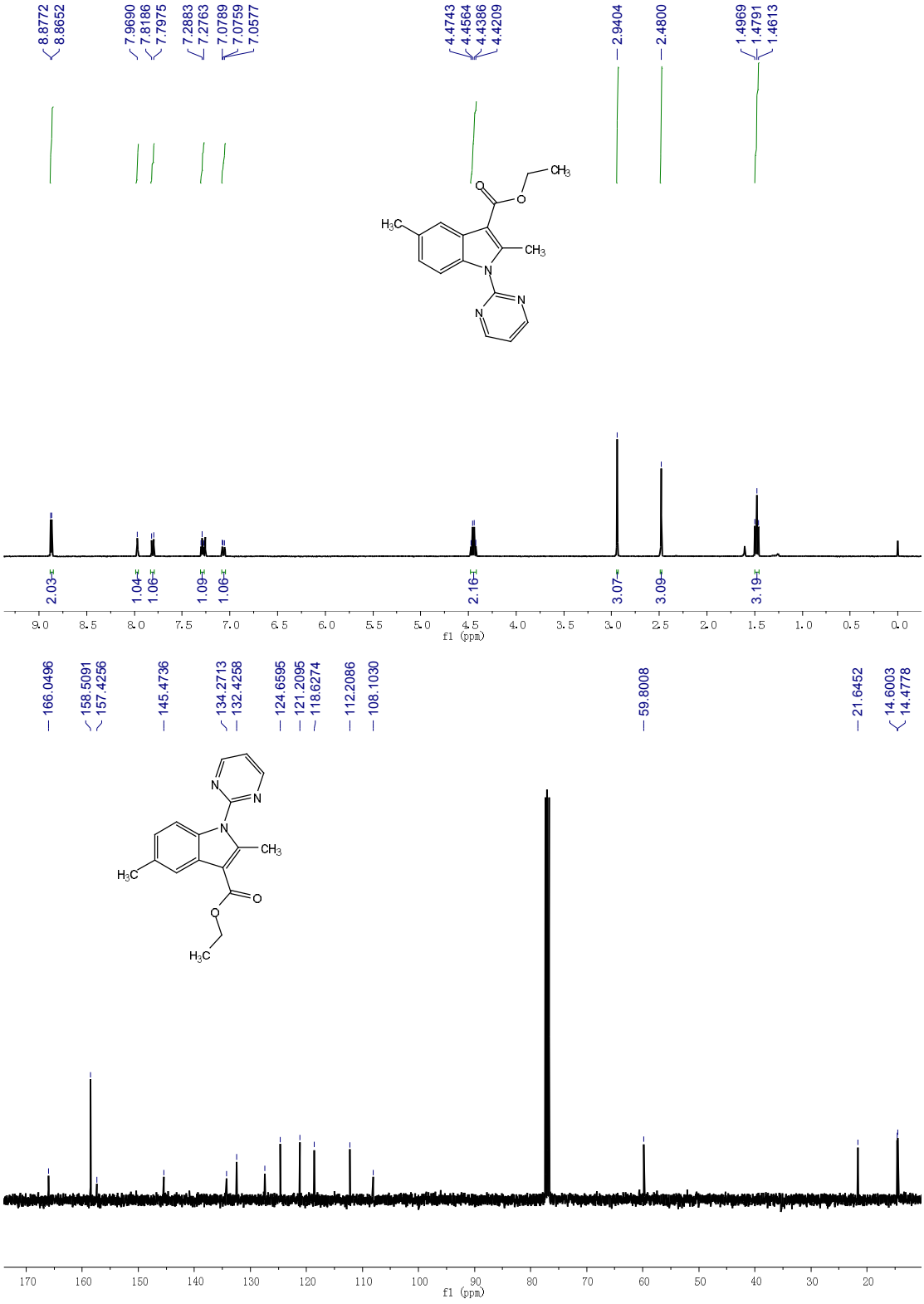
8.1884
8.1701
7.9141
7.8947
7.2900
7.2790
7.2696
7.2496
4.4712
4.4548
4.4374
4.4209
2.9503
1.4942
1.4771
1.4600
2.00
1.02
1.01
3.34
2.04
3.15
3.13
f1 (ppm)
165.9576
158.5759
157.2989
145.5935
135.9774
127.1856
122.9853
121.4140
118.8413
112.4618
108.3291
59.8525
14.5854
14.3443
f1 (ppm)

3sa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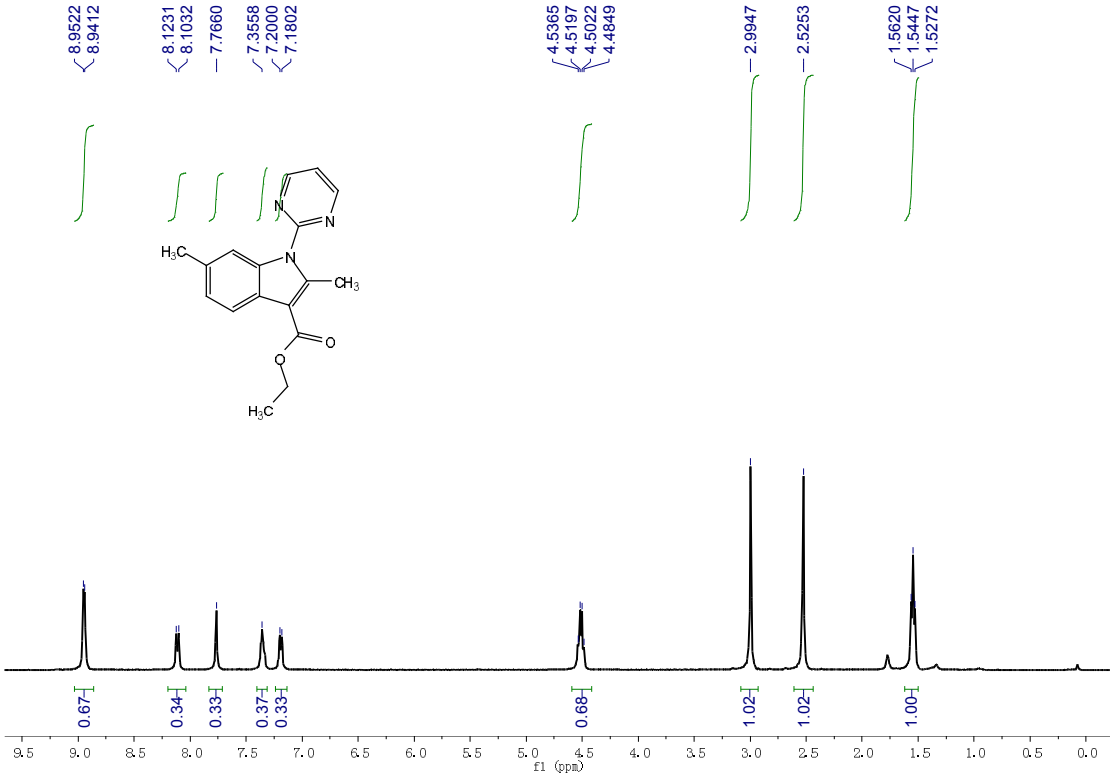
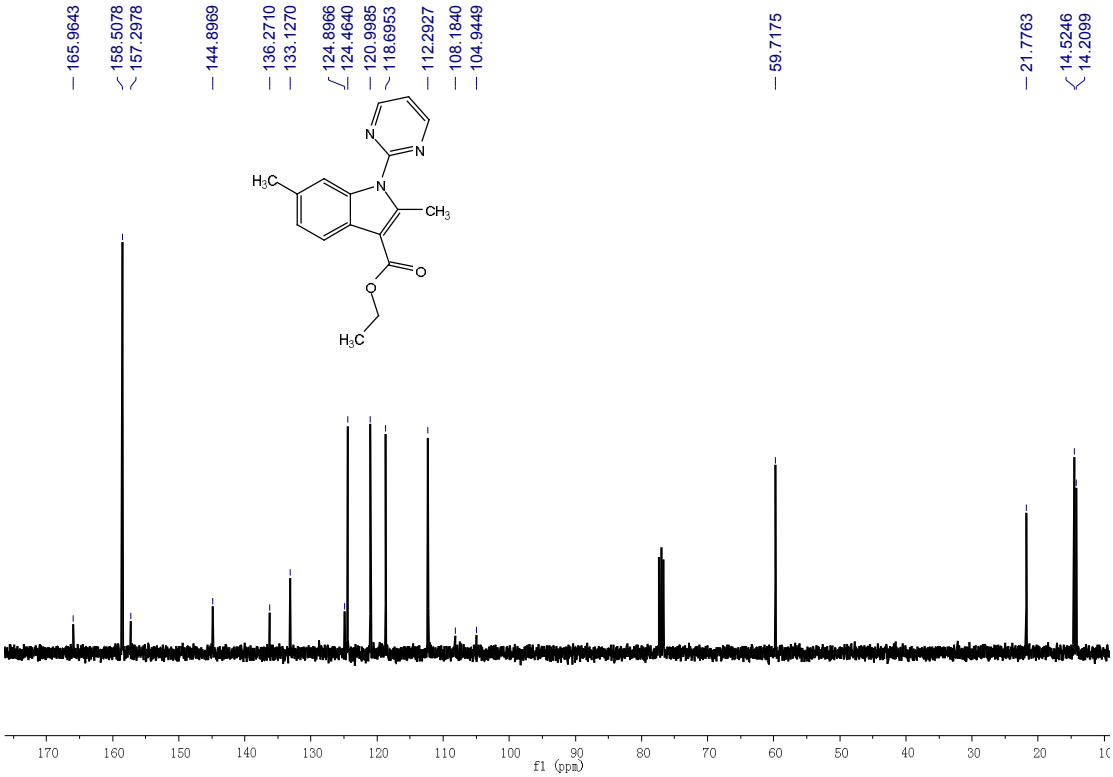
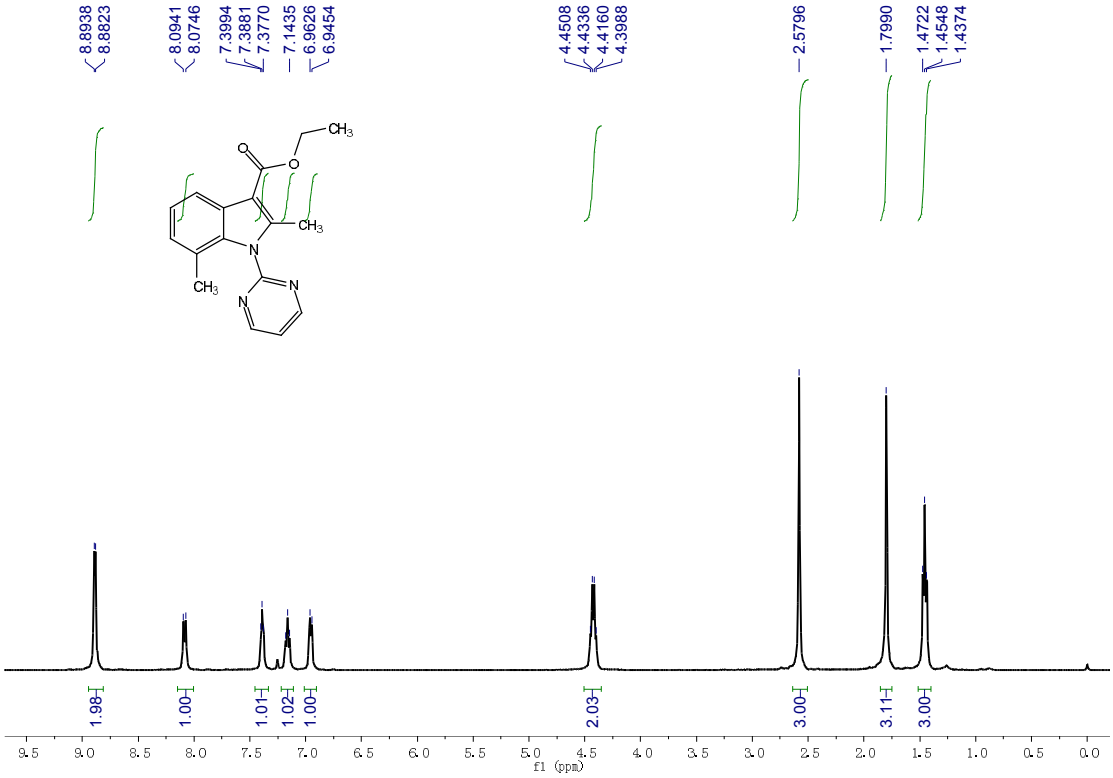
8.8652
7.9690
7.8186
7.7975
7.2883
7.2763
7.0789
7.0759
7.0577
4.4743
4.4564
4.4386
4.4209
2.9404
2.4800
1.4969
1.4791
1.4613
2.03
1.04
1.06
1.09
1.06
2.16
3.07
3.09
3.19
f1 (ppm)
166.0496
158.5091
157.4256
145.4736
134.2713
132.4258
124.6595
121.2095
118.6274
112.2086
108.1030
59.8008
21.6452
14.6003
14.4778
f1 (ppm)

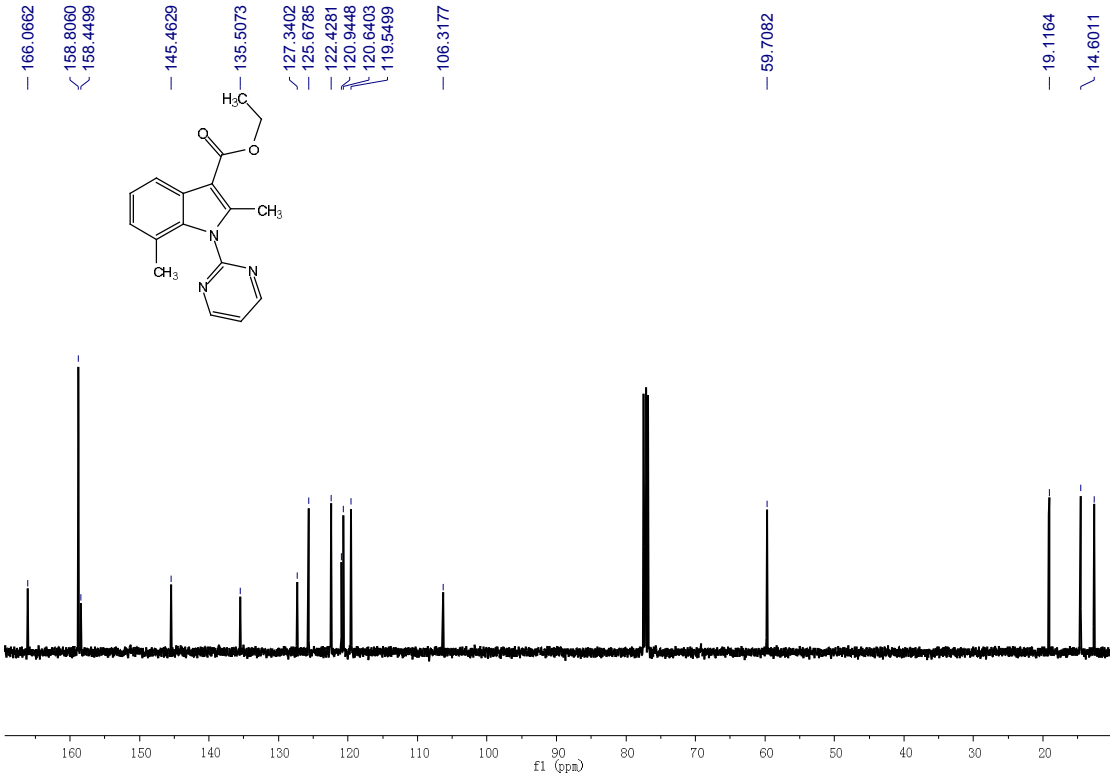
3ta


8.9522
8.9412
8.1231
8.1032
7.7660
7.3558
7.2000
7.1802
4.5365
4.5197
4.5022
4.4849
2.9947
2.5253
1.5620
1.5447
1.5272
0.67
0.34
0.33
0.37
0.33
0.68
1.02
1.02
1.00
f1 (ppm)

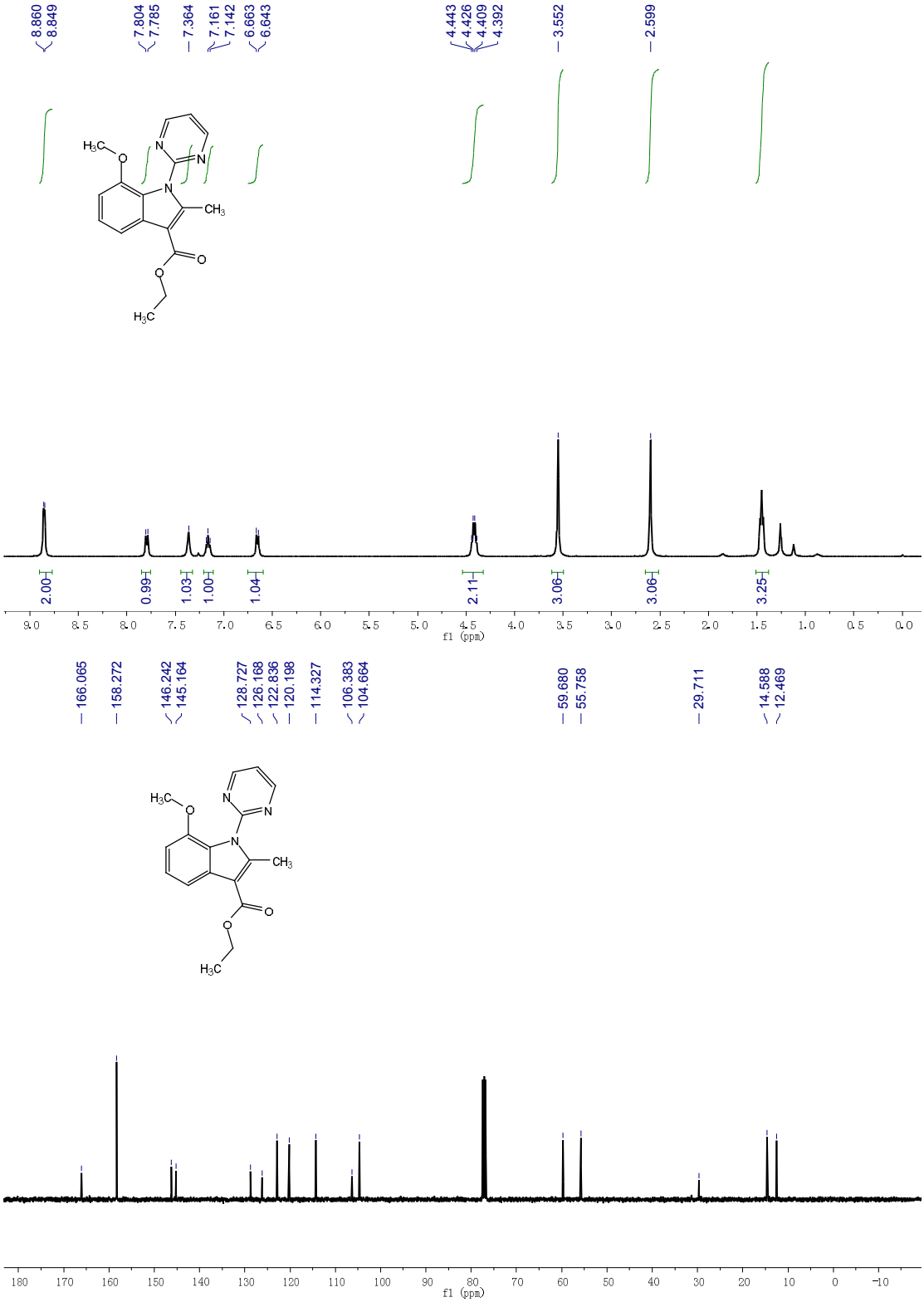

165.9643
158.5078
157.2978
144.8969
136.2710
133.1270
124.8966
124.4640
120.9985
118.6953
112.2927
108.1840
104.9449
59.7175
21.7763
14.5246
14.2099
f1 (ppm)

3ua

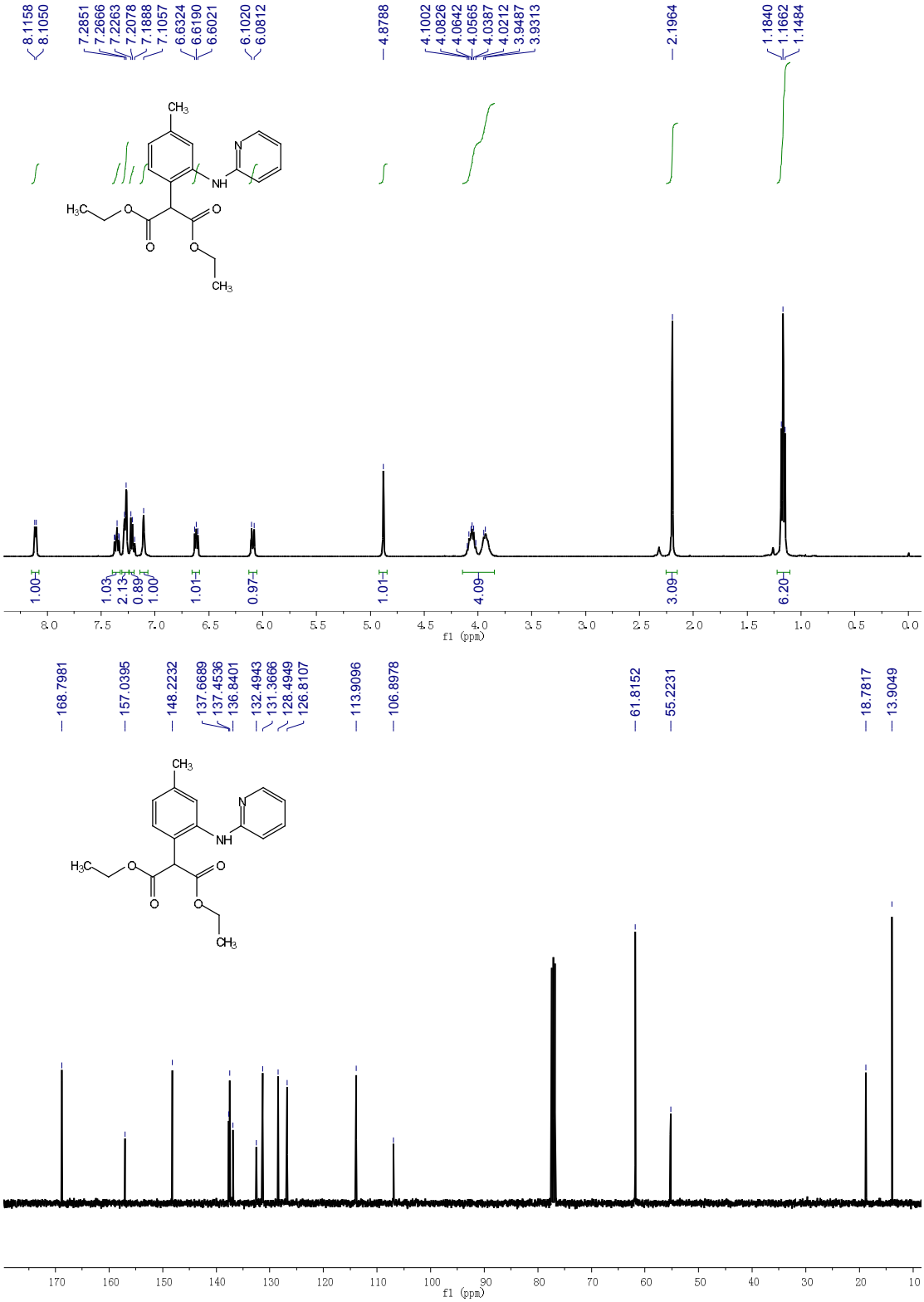

8.8938
8.8823
8.0941
8.0746
7.3994
7.3881
7.3770
7.1435
6.9626
6.9454
4.4508
4.4336
4.4160
4.3988
2.5796
1.7990
1.4722
1.4548
1.4374
1.98
1.00
1.01
1.02
1.00
2.03
3.00
3.11
3.00
f1 (ppm)


166.0662
158.8060
158.4499
145.4629
135.5073
127.3402
125.6785
122.4281
120.9448
120.6403
119.5499
106.3177
59.7082
19.1164
14.6011
f1 (ppm)

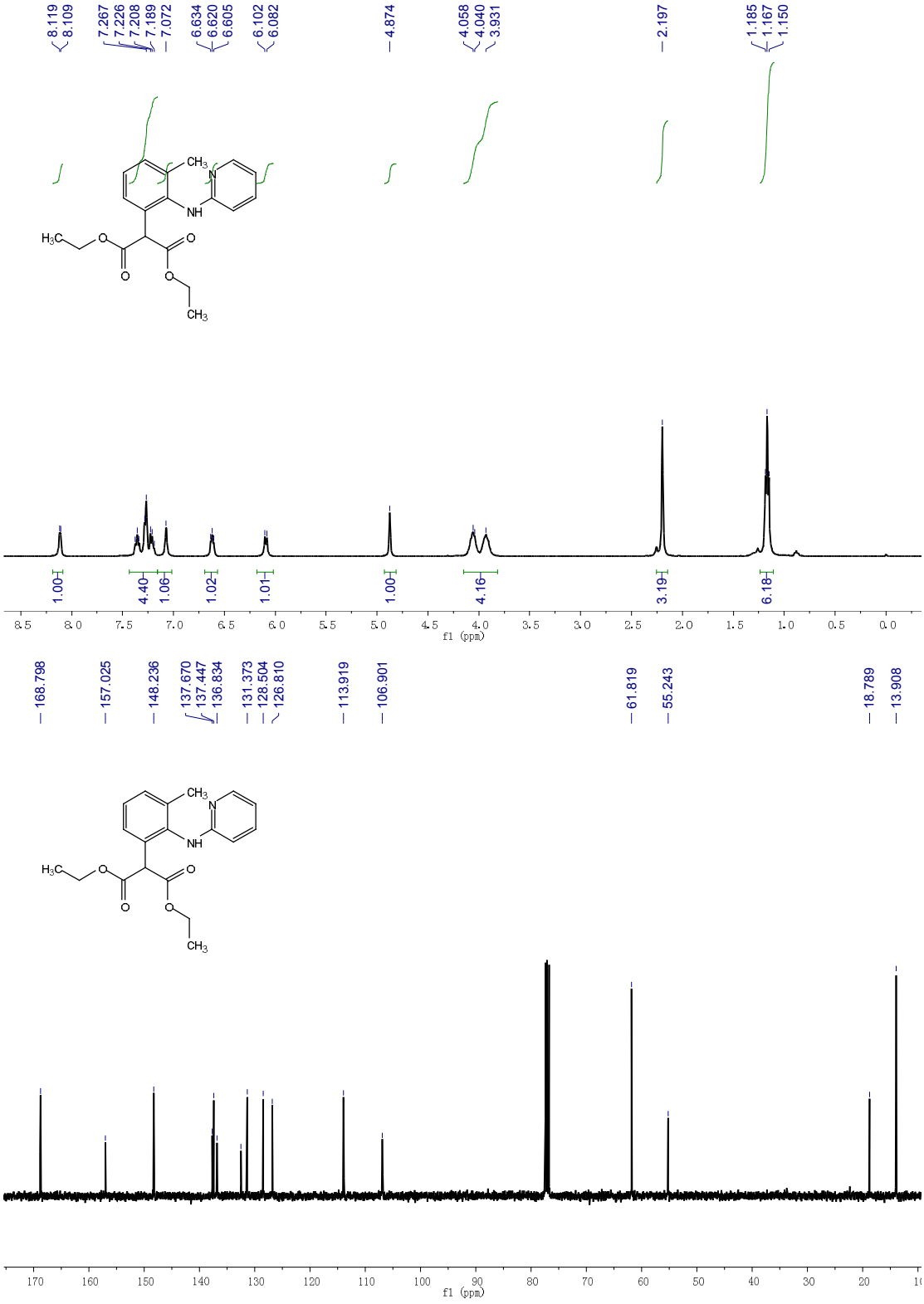
3va


8.860
8.849
7.804
7.785
7.364
7.161
7.142
6.663
6.643
4.443
4.426
4.409
4.392
3.552
2.599
2.00
0.99
1.03
1.00
1.04
2.11
3.06
3.06
3.25
f1 (ppm)
166.065
158.272
146.242
145.164
128.727
126.168
122.836
120.198
114.327
106.383
104.664
59.680
55.758
29.711
14.588
12.469
f1 (ppm)

5ba


8.1158
8.1050
7.2851
7.2666
7.2263
7.2078
7.1888
7.1057
6.6324
6.6190
6.6021
6.1020
6.0812
4.8788
4.1002
4.0826
4.0642
4.0565
4.0387
4.0212
3.9487
3.9313
2.1964
1.1840
1.1662
1.1484
CH3
NH
N
O
H3C
1.00
1.03
2.13
0.89
1.00
1.01
0.97
1.01
4.09
3.09
6.20
f1 (ppm)
168.7981
157.0395
148.2232
137.6689
137.4536
136.8401
132.4943
131.3666
128.4949
126.8107
113.9096
106.8978
61.8152
55.2231
18.7817
13.9049

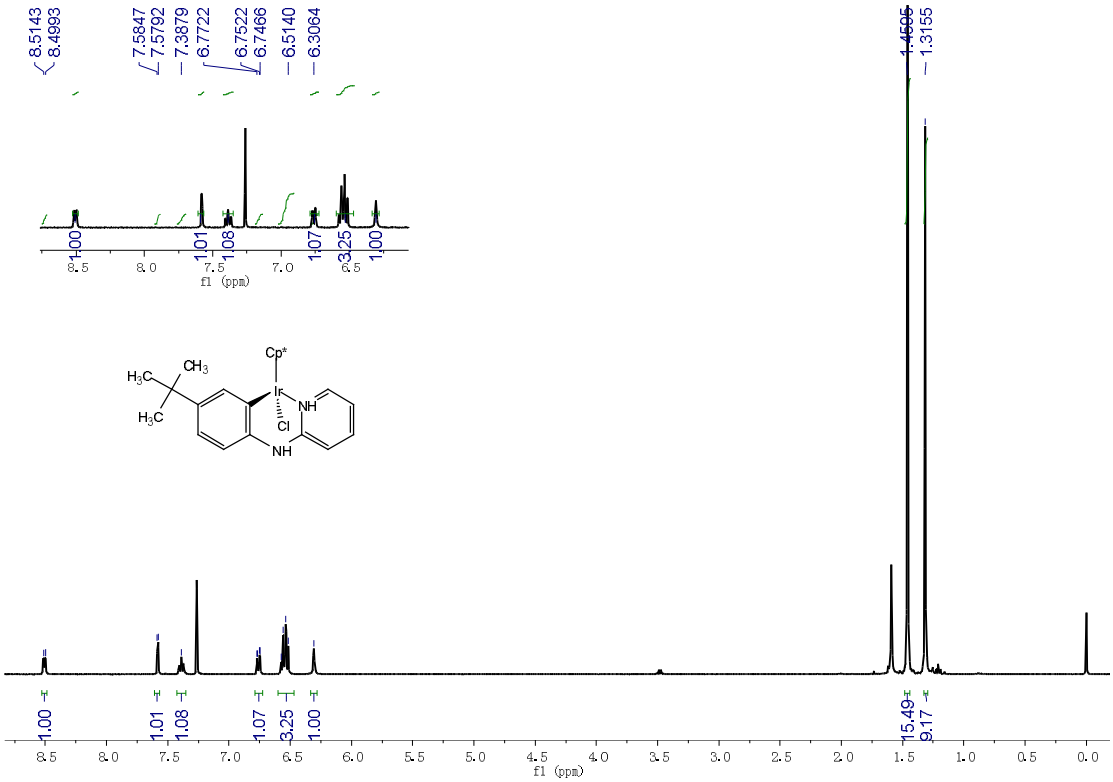
5ma

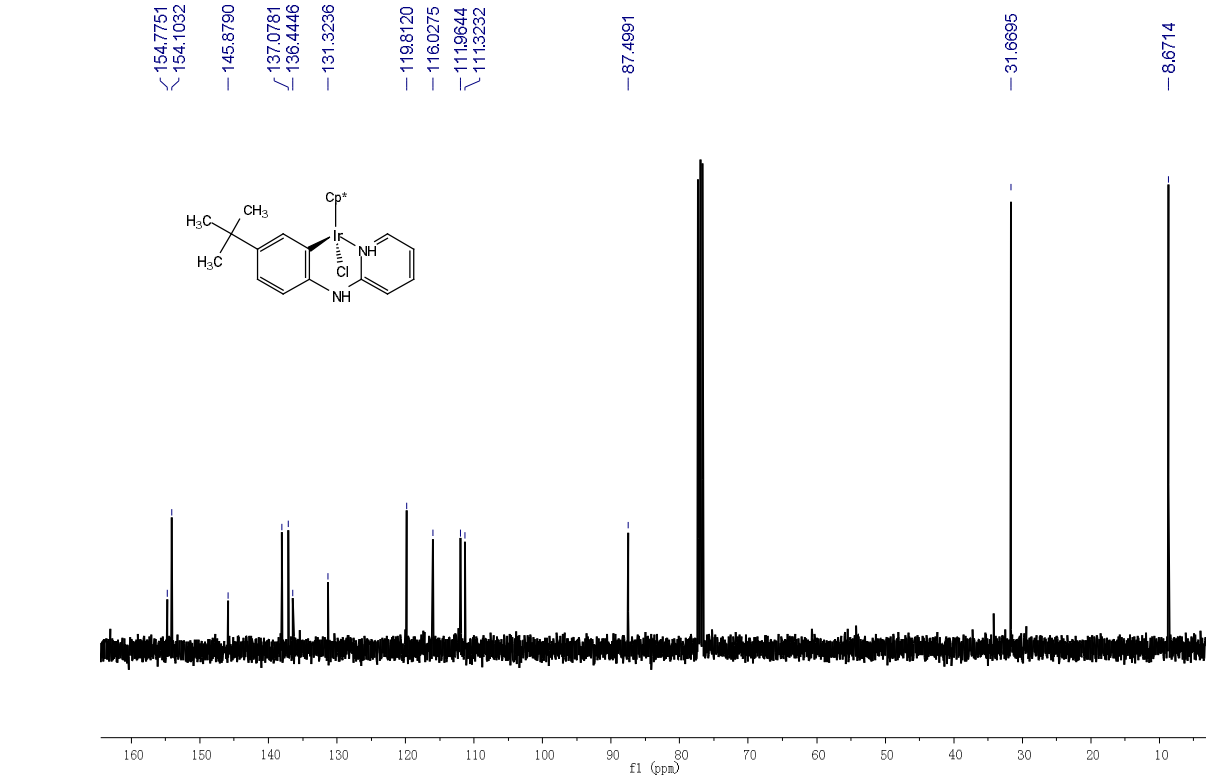

8.119
8.109
7.267
7.226
7.208
7.189
7.072
6.634
6.620
6.605
6.102
6.082
4.874
4.058
4.040
3.931
2.197
1.185
1.167
1.150
CH3
N
NH
H3C
O
O
O
O
CH3
1.00
4.40
1.06
1.02
1.01
1.00
4.16
3.19
6.18
f1 (ppm)
168.798
157.025
148.236
137.670
137.447
136.834
131.373
128.504
126.810
113.919
106.901
61.819
55.243
18.789
13.908
f1 (ppm)

6


8.279
7.972
7.952
7.069
7.051
7.031
4.416
4.398
4.380
4.363
2.707
2.438
1.455
1.437
1.419
H3C
NH
CH3
O
O
H3C
0.86
1.00
2.04
2.11
3.13
3.14
3.16
f1 (ppm)
166.235
143.327
134.883
132.152
124.953
123.310
120.952
110.520
104.490
59.459
21.597
14.619
14.188
H3C
NH
CH3
O
O
H3C
f1 (ppm)

7


8.5143
8.4993
7.5847
7.5792
7.3879
6.7722
6.7522
6.7466
6.5140
6.3064
1.4695
1.3155
1.00
1.01
1.08
1.07
3.25
1.00
15.49
9.17
f1 (ppm)
Cp*
CH3
H3C
H3C
Ir
NH
Cl
NH


154.7751
154.1032
145.8790
137.0781
136.4446
131.3236
119.8120
116.0275
111.9644
111.3232
87.4991
31.6695
8.6714
Cp*
CH3
H3C
H3C
Ir
NH
Cl
NH
f1 (ppm)